AD-A224 576

AFWAL-TR-87-2042
Volume XIII

PRODUCTION OF JET FUELS FROM COAL-DERIVED LIQUIDS

VOL XIII - Evaluation of Storage and Thermal Stability of Jet Fuels Derived from Coal Liquids

G. P. Sturm, Jr., R. D. Grigsby, J. W. Goetzinger, J. B. Green, and R. P. Anderson

IIT Research Institute
National Institute for Petroleum and Energy Research
P. O. Box 2128
Bartlesville, OK 74005

May 1990

INTERIM REPORT FOR THE PERIOD AUGUST 1988 - DECEMBER 1989

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION IS UNLIMITED

AERO PROPULSION AND POWER LABORATORY
WRIGHT RESEARCH AND DEVELOPMENT CENTER
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433-6563

NOTICE

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely Government-related procurement, the United States Government incurs no responsibility or any obligation whatsoever. The fact that the Government may have formulated or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication, or otherwise in any manner construed, as licensing the holder, or any other person or corporation; or as conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

This report is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

Will E. Harrison III

WILLIAM E. HARRISON III
Project Engineer

Charles L Delaney

CHARLES L. DELANEY, CHIEF
Fuels Branch
Fuels and Lubrication Division

FOR THE COMMANDER

Leo S Harootyan Jr

Leo S. Harootyan, Jr. Assistant Chief
Fuels and Lubrication Division
Aero Propulsion & Power Laboratory

If your address has changed, if you wish to be removed from our mailing list, or if the addressee is no longer employed by your organization, please notify AFWAL/POSF, WPAFB, OH 45433-6563 to help us maintain a current mailing list.

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION Unclassified	1b. RESTRICTIVE MARKINGS None
2a. SECURITY CLASSIFICATION AUTHORITY N/A 2b. DECLASSIFICATION/DOWNGRADING SCHEDULE N/A	3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited
4. PERFORMING ORGANIZATION REPORT NUMBER(S) N/A	5. MONITORING ORGANIZATION REPORT NUMBER(S) AFWAL-TR-87-2042, Vol XIII
6a. NAME OF PERFORMING ORGANIZATION National Institute for Petroleum and Energy Research 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Wright Research and Development Center Aero Propulsion and Power Laboratory
6c. ADDRESS (City, State, and ZIP Code) Post Office Box 2128 Bartlesville, OK 74005	7b. ADDRESS (City, State, and ZIP Code) Wright-Patterson AFB OH 45433-6563
8a. NAME OF FUNDING/SPONSORING ORGANIZATION 8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER FY1455-86-N0657
8c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. 63216F; PROJECT NO. 2480; TASK NO 16; WORK UNIT ACCESSION NO. 01

11. TITLE (Include Security Classification)
PRODUCTION OF JET FUELS FROM COAL-DERIVED LIQUIDS, VOL XIII - EVALUATION OF STORAGE AND THERMAL STABILITY OF JET FUELS DERIVED FROM COAL LIQUIDS

12. PERSONAL AUTHOR(S)
G. P. Sturm, Jr., R. D. Grigsby, J. W. Goetzinger, J. B. Green, and R. P. Anderson

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Interim	FROM 88-8 TO 89-12	May 1990	63

16. SUPPLEMENTARY NOTATION

17. COSATI CODES		
FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
Jet Fuel; Turbine Fuel; JP-8, Great Plains Gasification Plant, Coal Liquids; Storage Stability; Thermal Stability; Mass Spectrometry; Sediment Analysis; Deposit Analysis

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

In September 1986, the Fuels Branch of the Aero Propulsion Laboratory of Wright-Patterson Air Force Base, Ohio, commenced an investigation of the potential of the production of jet fuel from the liquid by-products streams produced by the gasification of lignite at the Great Plains Gasification Plant (GPGP) in Beulah, North Dakota. Funding was provided to the Department of Energy (DOE), Pittsburgh Energy Technology Center (PETC), to administer the experimental portion of this effort. This report details the program with the National Institute for Petroleum and Energy Research (NIPER) of the IIT Research Institute to study the storage and thermal stability of a JP-8 fuel produced from the GPGP liquid by-products streams. Sediments and deposits from stability tests were analyzed by IR and probe microdistillation/high resolution mass spectroscopy. Results were compared with corresponding results from a conventional petroleum-derived JP-8 fuel.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT [X] UNCLASSIFIED/UNLIMITED [ ] SAME AS RPT. [ ] DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED
22a. NAME OF RESPONSIBLE INDIVIDUAL William E. Harrison III	22b. TELEPHONE (Include Area Code) (513) 255-6601 — 22c. OFFICE SYMBOL AFWAL/POSF

DD Form 1473, JUN 86 — Previous editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE
UNCLASSIFIED

DISCLAIMER

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process or service by trade name, mark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

FOREWORD

In September 1986, the Fuels Branch of the Aero Propulsion Laboratory at Wright-Patterson Air Force Base, Ohio, commenced an investigation of the potential for production of jet fuel from the liquid by-product streams produced by the gasification of lignite at the Great Plains Gasification Plant located in Beulah, North Dakota. Funding was provided to the Department of Energy (DOE) Pittsburgh Energy Technology Center (PETC) to administer the experimental portion of this effort. This report details the effort of the National Institute for Petroleum and Energy Research of the IIT Research Institute (NIPER/IITRI), who, as a contractor to DOE (DOE Contract Number DE-FC22-83FE60149 studied the storage and thermal stabilities of a JP-8 fuel produced from the GPGP liquid by-product streams. DOE/PETC was funded through Military Interdepartmental Purchase Request (MIPR) FY1455-86-N0657. Mr. William E. Harrison III was the Air Force Program Manager, Mr. Gary Steigel and Dr. Nand Narain were the DOE/PETC Program Managers, and Dr. Raymond P. Anderson was the NIPER/IITRI Program Manager.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

LIST OF TABLES (contd)

LIST OF TABLES (contd)

EXECUTIVE SUMMARY

Results from a study of the storage and thermal stabilities of a JP-8 fuel produced from the Great Plains Gasification Plant liquid by-products streams were compared with similar results for a conventional petroleum-derived JP-8 fuel. Initial characterization and simulated distillation data for the two fuels indicated the coal-derived fuel contained more lower boiling material, a slight color, a high filtration time, and a high particulate content (the latter three properties being due to some suspended clay, most likely). Nevertheless, for the most part both fuels met specification tests for JP-8.

Both fuels exhibited good oxidation stability according to test ASTM D 2274 with the coal-derived fuel showing less sediment and color formation but somewhat higher peroxide content. Storage stability tests (aging at 80° C under 100 psig oxygen) gave the same results on both fuels through 3 weeks of aging. However, between the third and fourth weeks the coal-derived fuel deteriorated rapidly and exceeded the petroleum-derived reference fuel in color and sediment formation as well as peroxide content.

After separation of the coal-derived fuel into acid, base, and neutral fractions, storage stability tests on the neutrals, neutrals + acids, neutrals + bases, and neutrals + acids + bases (reconstituted fuel) showed large amounts of sediments formed after 4 weeks aging in each case with the neutrals alone producing the largest quantity.

Both fuels easily met specifications in terms of thermal stability testing with the coal-derived fuel showing a higher breakpoint temperature. Extended JFTOT (Jet Fuel Thermal Oxidation Test) runs were conducted at temperatures slightly above the breakpoints to generate filterable sediment and tube deposit samples for analyses.

Infrared analysis of a sample of sediment from the coal-liquid derived JP-8 fuel storage stability tests was not very definitive; however, the spectrum was very similar to that of the acid fraction separated from the fresh fuel. Separation of the sediment sample using NIPER's HPLC acid subfractionation method indicated the sediment was composed primarily of carboxylic acids and difunctional acids.

Mass spectra of the filterable sediments and JFTOT-tube deposits formed during extended thermal stressing runs of the coal-derived and petroleum-derived fuels were remarkably similar, indicating that the same or similar compound types were responsible for solids formation in both fuels.

When mass spectra of the filterable sediment from either fuel were compared with those of the tube deposit from the same fuel, a number of similarities were found as well as some significant differences. Both sets of spectra showed molecular- and fragment-ion peaks for aromatic and nonaromatic hydrocarbons and for compounds containing one to three

oxygens. Strong peaks were observed in the spectra of the filterable sediment corresponding to aromatic compounds containing one nitrogen. These peaks were much weaker or absent in the spectra from the tube deposit. No spectra of the sediment or tube deposit from either fuel showed any more than traces of sulfur-containing compounds.

An intense, nonaromatic fragment ion containing three oxygens was identified in the spectra of the tube deposits from both fuels. This ion was also found in the spectra of the filterable sediments from both fuels although its intensity was much weaker. The ion could not be correlated with a molecular ion from any particular compound type, but it may have originated from an alcohol, ether, or some other type that does not produce a significant molecular ion.

A 22-component hydrocarbon type mass spectral analysis method applied to fresh samples of the two fuels and samples of the fuels after stability testing was not sufficiently sensitive to detect any significant changes in the composition of either fuel. On the other hand, very significant differences were evident in the compositions of the petroleum-derived fuel and the coal-derived fuel when one was compared to the other. Field ionization mass spectral analysis of fresh samples of the two fuels gave results in good qualitative agreement with the 22-component method results. Comparison of the two methods on a quantitative basis was not possible because of the lack of sensitivity factors for the FI/MS data. However, the FI/MS analysis did indicate relatively high concentrations of components with carbon numbers less than twelve in both fuels which are outside the range C_{12} to C_{36} for which the 22-component method is strictly applicable.

Although neither the analyses of the fresh, aged, and stressed fuels nor the structural information obtained through mass-spectral analysis of the filterable sediments and tube deposits led to identification of any specific precursors responsible for solids formation in the two fuels in the study, the results presented do demonstrate the potential of the methods for studying the mechanisms leading to fuel degradation under conditions of high temperature, such as those encountered in turbine engines.

INTRODUCTION

An investigation of the potential for production of jet fuel and other commercial products from the liquid by-product streams produced by the gasification of lignite at the Great Plains Gasification Plant (GPGP) located in Beulah, North Dakota, was begun in September 1986 by the Fuels Branch of the Aero Propulsion Laboratory at Wright-Patterson Air Force Base, Ohio. The GPGP produces about 14.5 MM SCF/D of substitute natural gas, 2900 B/D of tar oil, 830 B/D of crude phenols, and 650 B/D of naphtha from lignite. The liquid by-products are normally used as boiler fuel in the gasification plant. The Department of Energy and the U.S. Air Force began the program to investigate the potential for increasing the economic viability of the plant and, at the same time, create a reliable, constant source of jet fuel for Air Force bases in the northern great plains area (1). As part of the overall program, the National Institute for Petroleum and Energy Research, which is operated by the IIT Research Institute under contract with the Department of Energy has investigated the storage and thermal stability of a JP-8 fuel produced from the GPGP liquid by-products.

Several decades of fuel stability studies have increased our knowledge of the detailed chemistry causing degradation. Until recently, most of the studies were focused on trace components (2-4). However, our work on petroleum-derived jet fuels has shown that degradation will continue even on neutral fractions of relatively clean samples (5). In most research, ambient storage stability and high temperature thermal stability are viewed as two separate issues. When trace contaminants are a primary consideration, that may be appropriate. However, our recent findings indicate that hydrocarbons susceptible to degradation/oxidation at high temperatures are also the initiators of ambient reactions.

The hydrocarbon compound type that seems to be emerging as one of particular importance to fuel degradation is the cycloalkylaromatics (such as tetralin) with a non-hydrogen entity alpha to the aromatic ring. Of course, this type of compound structure is present at significant levels in many coal liquids including the hydrotreated tar oil distillates from the GPGP. Thus, determination of the storage and thermal stabilities of jet fuel produced from the GPGP liquid by-products is important in evaluating the quality of the fuel. In addition, such samples would be of immense interest in providing further information on fuel stability in relation to composition.

OBJECTIVES

1. To determine the relative storage and thermal stabilities of a JP-8 fuel derived from the GPGP liquid by-product streams and a conventional petroleum-derived JP-8 fuel.

2. To investigate the detailed chemistry relating fuel composition with storage and thermal stabilities.

APPROACH

The approach for this investigation is outlined in the following tasks.

Task 1. Initial Sample Characterization

Limited initial testing was performed to determine the degree of degradation that may have occurred since prior characterization elsewhere and to provide the baseline for the subsequent studies. This testing included simulated distillation (ASTM D 2887), particulate content (ASTM D 2776), filtration time, color, and viscosity.

Task 2. Storage Stability

The storage stability of the samples was determined by two different methods. In the first, the samples were aged at 80° C under 100 psig oxygen for 1, 2, 3, and 4 weeks. The resulting aged samples were analyzed for filterable and adherent solids, color, and peroxides. Similarly, samples were aged by the current specification oxidation test (D 2274) in which oxygen is bubbled through the sample for 16 hours while in a bath at 95° C. A similar workup was performed, so that results could be compared directly.

In addition, the coal liquid-derived jet fuel was separated into acids, bases, and neutrals. Samples of the acids and bases reconstituted with the neutrals, individually and together, were aged by the first method. In addition, samples of coal-liquid-derived jet fuel were mixed with the petroleum-derived jet fuel and aged by the first method.

Task 3. Thermal Stability

Each of the samples was individually assessed for thermal stability by running ASTM D 3241 at 260° C. Breakpoint determination runs were made on each sample to find the temperature at which degradation becomes significant. The samples were then stressed for extended periods of time at a temperature approximately 10° C above the breakpoint temperature to generate sufficient solids on the heated tube and on the downstream filter to permit mass spectral analyses of the solids.

Task 4. Solids Analyses

Solids generated in Tasks 2 and 3 were characterized by infrared spectroscopy, separation procedures, and probe microdistillation/high resolution mass spectrometry in an attempt to determine their similarity to analogous petroleum degradation products and provide as much detailed compositional information as possible.

Task 5. Liquid Fuel Analyses

Limited analyses by high resolution electron impact and field ionization mass spectrometry were performed on the liquid fuel samples before and after aging/thermal stressing in an attempt to obtain degradation mechanism information.

Task 6. Reporting

This final report presenting all of the information obtained and an interpretation of that data in relation to fuel stability is the final task of this project.

RESULTS AND DISCUSSION

The experimental results and discussion are given below in accordance with the project tasks.

Task 1. Initial Sample Characterization

Initial characterization and simulated distillation data for the JP-8 fuel produced from GPGP coal-derived liquids (No. 89-WEH-157) designated NIPER Number 2987 are shown in table 1 and figure 1, respectively, along with corresponding data from the reference petroleum-derived JP-8 fuel. The coal-derived fuel showed a very slight color which may have been due, at least in part, to suspended clay, which in turn is the most logical explanation for the high filtration time and particulate content observed. Both fuels passed the viscosity specification easily. In addition, both fuels met the distillation specification except for slightly exceeding the maximum value for the endpoint temperature. Also, the coal-derived JP-8 did show more low-boiling material than the reference fuel as can be seen in figure 1. (Copies of the complete simulated distillation data are given in Appendix A.) No peroxides were detected in the reference fuel, but the coal-derived JP-8 showed a trace (0.5 ppm).

TABLE 1. - Initial characterization data for coal-liquid-derived (#2987) and petroleum-derived (REF) JP-8 fuels

Property	Method	Fuel		Specification
		REF.	#2987	Maximum
Color, Saybolt	D 156	+29	+14	TBR
Viscosity, -20°C, cSt	D 445	4.8	4.4	8.0
Particulate, mg/L	D 2276	0.26	1.2	1.0
Filtration, time, min.	MIL-T-83133B Appendix A	6.5	28	15
Peroxide, ppm	D 3703	0	0.5	-

Task 2. Storage Stability

Oxidation stability test (ASTM D 2274) results for the two fuels are summarized in table 2. The coal-liquid-derived fuel (No. 2987) showed less sediment formation and color formation than the reference fuel. Peroxide values for fuel 2987 were somewhat higher than the reference fuel values. The storage stability test results summarized in table 3 showed lower sediment formation and color values for the coal-derived fuel through 3 weeks of storage at 80° C under 100 psig oxygen. However, the coal-liquid fuel peroxide values were consistently higher than the reference fuel values and reached a maximum value at approximately 3 weeks. Between 3 and 4 weeks the coal-derived fuel deteriorated significantly under these test conditions. A large quantity of sediment was formed, the fuel darkened, and the peroxide content decreased somewhat as has been observed with other fuels.

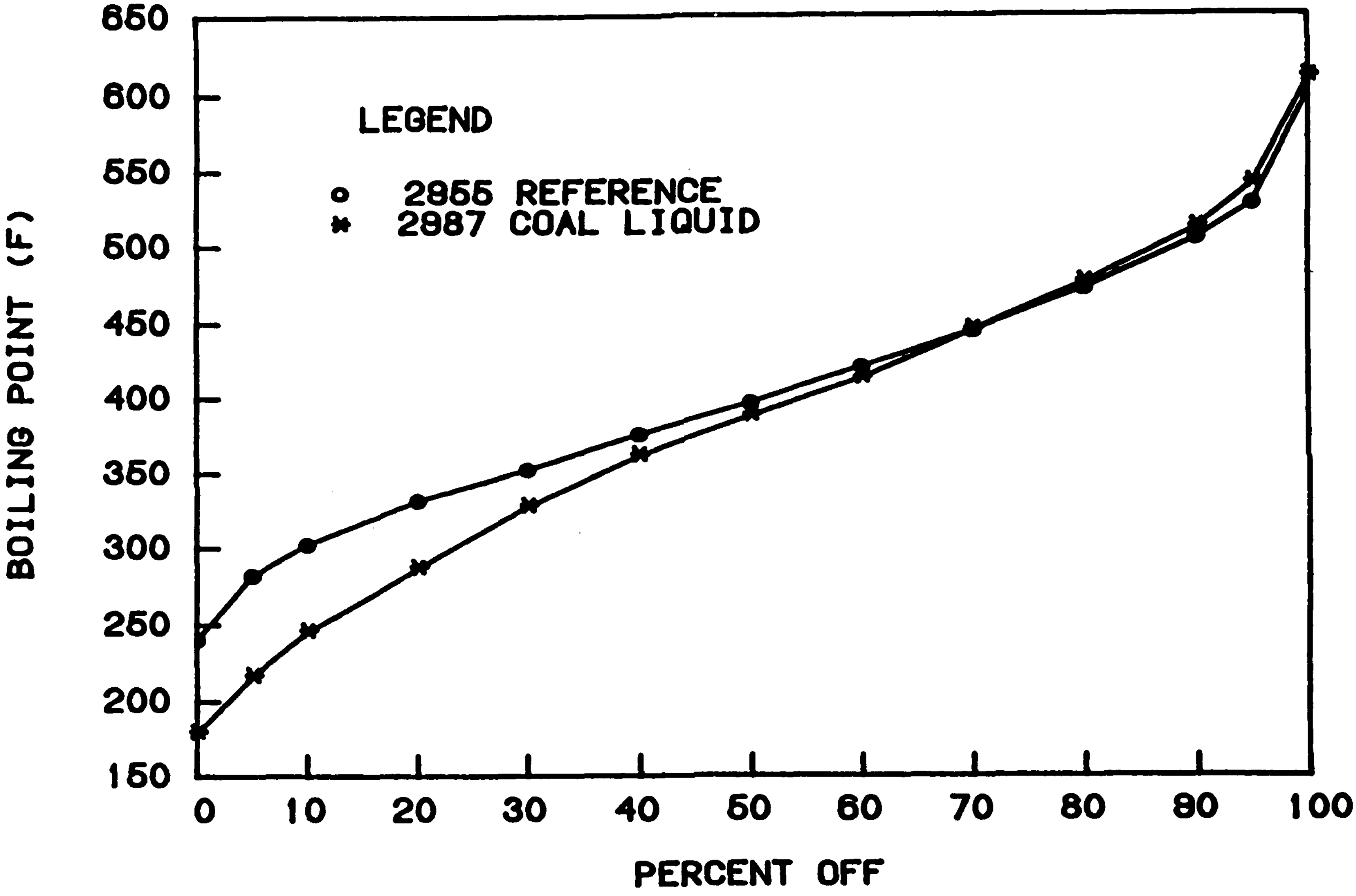

FIGURE 1. - Simulated distillation of JP-8 fuel.

TABLE 2. - Oxidation stability (ASTM D 2274) results for coal-liquid-derived (#2987) and petroleum-derived (REF) JP-8 fuels

Aging Time	16 hours Fuel		40 hours Fuel	
Property	REF.	#2987	REF.	#2987
Filterable sediment, mg/100 mL	0.02	0.03	0.25	0.02
Adherent sediment, mg/100 mL	0.20	0.00	0.22	0.00
Total sediment, mg/100 mL	0.22	0.03	0.47	0.02
Peroxide, ppm, D 3703	0.8	3.0	3.6	8.4
Color, D 1500	L0.5	L0.5	1.5	L0.5

TABLE 3. - Storage stability results for coal-liquid-derived (#2987) and petroleum-derived (REF) JP-8 fuels

Aging Time	1 Week Fuel		2 Weeks Fuel		3 Weeks Fuel		4 Weeks Fuel	
Property	REF	#2987	REF	#2987	REF	#2987	REF	#2987
Filterable Sediment mg/100 mL	0.8	0.3	1.3	0.5	1.5	1.0	2.7	9.1
Adherent Sediment mg/100mL	0.5	0.2	0.5	0.1	0.6	0.7	1.1	398
Total Sediment mg/100 mL	1.3	0.5	1.8	0.6	2.1	1.7	3.8	407
Peroxide, ppm D 3703	3.5	9.5	6.6	39.0	8.9	757	12.8	334
Color, D 1500	L1.0	L0.5	L1.0	L0.5	L1.0	L0.5	L1.0	2.5

In order to determine the compound class(es) responsible for sediment formation in aging experiments with fuel 2987, duplicate samples of the fresh fuel were separated into acids, bases, and neutrals for aging experiments with reblended samples. The acid and base fraction yields are given in table 4.

TABLE 4. - Acid and base fraction yields for separation of fuel 2987, Wt %

Sample No.	Acid	Base	Neutral	Recovery
1	0.0436	0.0135	98.38	98.43
2	0.0382	0.0222	97.59	97.65
Average	0.0409	0.0178	97.98	98.04

In preparing the blends, the quantity of acid or base added to the neutral fraction was such that the concentration of acid or base in the blend would be the same as in the whole fuel. However, the acid fraction did not completely dissolve in the neutral fraction, even after several hours in an ultrasonic bath at 50° C. The blends were filtered and the amount of undissolved acid (or base) determined. The actual concentration of acid or base was then calculated and is shown in table 5. The base appeared to be dissolved completely; the amount of undissolved material on the filter was insignificant.

TABLE 5. - Concentration of Acid or Base in Blends

Sample	Concentration, wt %
Neutral + Acid, Bottle A:	0.0337 Acid
Bottle B:*	0.0323 Acid
Neutral + Base: (Both bottles)	0.0337 Base
Neutral + Acid + Base: (Both bottles)	0.0337 Acid 0.0178 Base

*The second bottle of the first blend broke when it was pressurized. Consequently, a second blend was prepared for the second bottle.

In addition to the reblended samples described in table 5, samples of fuel 2987 neutrals, fresh whole fuel 2987, and two blends of fuel 2955 (the petroleum-derived JP-8 fuel) in fuel 2987 were prepared for aging at 80° C under 100 psig oxygen pressure in borosilicate glass pressure vessels for 4 or 5 weeks. The samples are listed below:

Samples Aged:

2987, Neutral
2987, Neutral + Acid
2987, Neutral + Base
2987, Neutral + Acid + Base
2987, Whole fuel

Blend 1: 25% # 2955 + 75% # 2987
Blend 2: 75% # 2955 + 25% # 2987

Samples were aged in duplicate for all samples except the last two. The volume of sample in each pressure vessel was 100 mL; the total capacity of the vessels was approximately 200 mL. Results from the aging experiments are summarized in tables 6 and 7. Aging time was 4 weeks except where noted otherwise.

It is noteworthy that the induction period before formation of significant quantities of sediment in the whole fuel was about 1 week longer than for similar experiments conducted earlier. This slower reaction rate may have been caused by a slightly different oven temperature, or by some other unknown factor.

The neutral + acid results show a large difference between duplicates. The duplicate samples were not identical as sample A was prepared using separation Run 1 acids and B was prepared using Run 2 acids. Also, sample B was placed in the oven several days after sample A. Whether the small difference in composition between samples A and B, possible small differences in aging conditions, or some other unknown factor was responsible for the different rate of sediment formation could not be determined. The differences observed between other duplicate sets are not surprising considering the rate at which the sediment forms once it starts to form.

TABLE 6. - Sediment and peroxide formation in aged blends

Blend	Bottle	Sediment, mg/100 mL			Peroxide
		Filterable	Adherent	Total	Number (ppm)
# 2987 Neutral	A	7.1	268.8	275.9	400
	B	19.4	553.3	572.7	195
	Avg.			424.3	
# 2987 Neutral + Acid	A	1.7	11.1	12.8	846
	B	21.2	121.1	142.3	1242
	Avg.			77.5	
# 2987 Neutral + Base	A	5.3	134.3	139.6	746
	B	5.9	250.4	256.3	411
	Avg.			197.9	
# 2987 Neutral + Acid + Base	A	5.3	143.5	148.8	1323
	B	4.9	170.6	175.5	1023
	Avg.			162.1	
# 2987 Whole Fuel	A	0.7	0.2	0.9	243
	[1]B	10.9	239.3	250.1	1886
	Avg.	(different time periods)			
Blend: 25% 2955, 75% 2987[1]		1.6	0.8	2.4	13.4
Blend: 75% 2955, 25% 2987[1]		3.0	0.7	3.7	13.5

[1]Aged 5 weeks, since there was no visible sediment after 4 weeks.

TABLE 7. - Color of fresh and aged blends (by ASTM D 1500)

Blend		Fresh	Aged
2987 Neutral	A	0	2.5
	B	0	2.5
2987 Neutral + Acid	A	0.5	1.0
	B	0.5	L2.0
2987 Neutral + Base	A	L0.5	2.0
	B	L0.5	L2.5
2987 Neutral + Acid + Base	A	L1.0	L2.0
	B	L1.0	2.0
2987 Whole Fuel	A	L0.5	0.5
	[1]B	L0.5	L2.0
Blend: 25% 2955, 75% 2987[1]		Not measured	0.5
Blend: 75% 2955, 25% 2987[1]		Not measured	1.0

[1]Aged 5 weeks; all others aged 4 weeks.

It is interesting that the neutrals formed the largest amount of sediment. Smaller, but very significant, quantities of sediment were formed in samples of the neutrals with the acids, bases, and acids + bases reblended. Also of interest are the results for the two blends of the petroleum-derived and coal-liquid-derived fuels. In both samples, the sediment formation chemistry appears to be controlled by the petroleum-derived fuel even though its concentration varies from 25% to 75%. The sediment formation, peroxide content, and color value for each of these two blends are similar to the corresponding values for fuel 2955 as shown in table 3 (3.8 mg/100 mL, 12.8 ppm peroxide, and L1.0 color, aging time-4 weeks). The fact that the fuel 2955/fuel 2987 blend data are more comparable to those of fuel 2955 suggests that fuel 2955 may have contained an antioxidant additive or that some components of fuel 2955 are effective antioxidants. Note also that the fuel 2955/fuel 2987 blend data are after 5 weeks aging as compared to the earlier 4-week aging data for fuel 2955 alone.

Task 3. Thermal Stability

The JFTOT (ASTM D 3241) results for the petroleum-derived reference fuel (#2955) and the coal liquid-derived fuel (#2987) are summarized in table 8. Both fuels meet the specifications very easily. The coal-derived fuel is stable to a higher temperature (295° C) than the reference fuel (275° C) as determined by the breakpoint temperature tests.

TABLE 8. - Thermal stability (ASTM D 3241) results for coal-liquid-derived (#2987) and petroleum-derived (REF) JP-8 fuels

Conditions:

Tube Temp.	260° C (500° F)
Fuel Flowrate	3 mL/min.
Test Duration	2.5 hours

Property	Fuel REF	Fuel #2987	Specification
Tube Deposit Rating	1	1	3 maximum
Pressure drop, mm Hg	0.0	0.0	25 maximum
Breakpoint, ° C	275	295	260 minimum

For the extended runs to generate tube deposits and filtered sediments for mass spectrometric analyses, the fuel flow system of the JFTOT was modified so that the fuel flows from the heated test section through a 25-mm filter holder to the variable speed pump of the thermal fouling tester, then back to the spent fuel reservoir of the JFTOT. A fuel flow rate of 1 mL/min was used.

In the first extended test run for the reference fuel (#2955), a nylon filter with a pore size of 0.45 μm was used. The tube temperature was 280° C (5° C above breakpoint). The filter plugged and stopped the fuel flow after only 7 hours. The filter was washed with heptane and dried in a vacuum oven. The weight of sediment on the filter was 1.43 mg. The JFTOT tube was not weighed.

For the second extended run with the reference fuel, a glass fiber filter, Type GF/F, with a pore size of approximately 0.7 μm was used. All other experimental conditions were the same. A run of 10 hours gave no detectable plugging of the filter. However, when the system was disassembled, it was observed that the filter had partially disintegrated. The test filter was washed with heptane by placing it on top of a 47-mm nylon filter (pore size 0.8 μm). The weight of sediment on the glass fiber filter was determined to be 0.70 mg. However, it should be considered as a minimum value as some of the partially disintegrated filter may have been lost during the experiment. The stressed fuel was saved and stored in a freezer. The JFTOT tube with its deposit was not weighed but was saved for mass spectrometric analysis.

The extended JFTOT run with the coal-liquid-derived fuel was conducted at a tube temperature of 310° C (15° C above the breakpoint) using a 25 mm diameter nylon, 0.45 μm pore size filter. The fuel flowrate was again 1 mL/min. After 17 hours the filter plugged. A deposit of 0.4 mg on the tube and a 2.0 mg quantity of sediment on the nylon filter were obtained.

These materials have been analyzed and their compositions compared with the compositions of corresponding materials produced from the petroleum-derived reference JF-8 fuel as part of Task 4.

Task 4. Solids Analyses

Selected samples of sediments from the storage stability tests in Task 2 and JFTOT tube deposits and filtered solids from Task 3 were characterized by infrared spectroscopy, acid subfractionation, and probe microdistillation/high resolution mass spectrometry.

Infrared Analyses

A sample of the sediment produced upon aging the coal-liquid-derived JP-8 fuel (# 2987) at 80° C under 100 psi oxygen for 4 weeks was analyzed by infrared (IR) spectroscopy. The spectrum was compared to similar analyses of the acid fraction and base fraction separated from fresh fuel 2987. The spectra for the three samples are shown in figure 2. The following conclusions may be drawn from examination of the IR data.

a) An intense carbonyl band appears in each of the three spectra. Most of the peak shapes and frequencies for the sediment and the acid samples are similar.

b) Hydroxyl compounds are present in the acid and sediment samples. The base fraction may contain a small amount of hydroxyl compounds but interference from water in this sample precludes a definite conclusion.

Sediment Separation

A portion of the sediment sample above was further characterized by separation into six subfractions using NIPER's HPLC acid subfractionation method. Yields of the six subfractions, which are separated according to increasing acidity, are given in table 9 along with compound types typically present in each subfraction. Any neutral or basic compounds present in the sediment would be expected to separate into subfraction 1 along with the very weak acids. The low recovery experienced was attributed to loss of material in the work-up of subfraction 6 and possible retention of very polar material on the HPLC column. The yield data and the HPLC chromatogram shown in figure 3B show that the bulk of the sediment sample was separated into subfractions 5 and 6 which typically contain carboxylic acids and difunctional acids, respectively. Comparison of the sediment chromatogram (figure 3B) with the HPLC chromatogram of the acid fraction from the fresh fuel 2987 (shown in figure 3A), indicates the fuel acid fraction contains much more weak acid material and the chromatograms show some similarity in the strong acid region corresponding to subfractions 5 and 6. Detailed GC/MS analyses of these two subfractions could aid in determining the exact compound types present, but was outside the scope of this project.

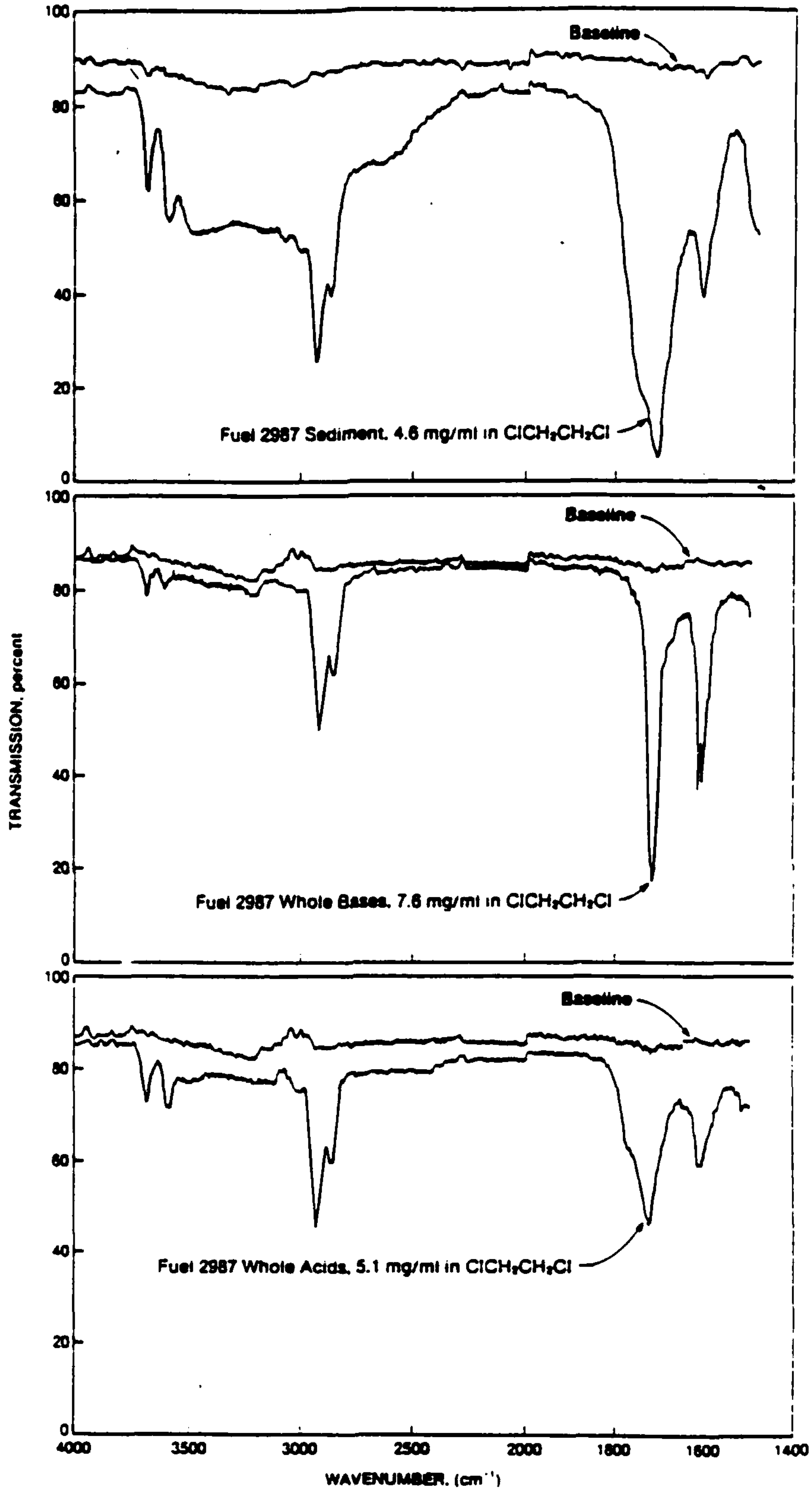

FIGURE 2. - IR spectra for fuel 2987 sediment, whole base and whole acid.

Table 9. - HPLC separation of fuel 2987 sediment: subfraction yields and typical compositions

Subfraction	Yield, wt %	Typical Composition
1	0.77	very weak acids, polynuclear aromatic hydrocarbons
2	1.21	2-3 ring pyrrolic benzologs
3	1.21	4-5 ring pyrrolic benzologs and hindered hydroxyaromatics
4	7.84	hydroxyaromatics
5	13.03	carboxylic acids
6	54.68	difunctional acids
Recovery	78.74	

Mass Spectral Analyses

The methods used in the analyses of the JFTOT tube deposits and filterable sediments from the reference and coal-derived fuels were developed recently at NIPER as part of a similar project conducted for the Naval Air Propulsion Center, Trenton, NJ (6,7). A mass-spectral technique, known as probe microdistilllation/mass spectrometry or PMD/MS, was used to provide high resolution mass spectra of the solids formed when the fuels were thermally stressed in the JFTOT apparatus (8).

Deposits on the JFTOT tubes were sampled by machining their surfaces in a lathe using a cleaned tool bit (6). Turnings containing each deposit were then placed in a temperature-programmed quartz probe for introduction under PMD/MS conditions into a Kratos MS-50 high resolution mass spectrometer (Kratos Analytical Instruments, Manchester, U.K.). Probe temperature was increased linearly at 10° C/min. Twenty to thirty spectra were recorded at a resolving power of 10,000 to 20,000 over a temperature range from ambient to greater than 400° C. Seventy eV electron impact was used for ionization to maximize the signal-to-noise ratio on mass-spectral peaks being formed from a limited amount of sample. Mass spectra were not recorded below m/z 70; therefore, some lower molecular-weight homologues are not included in the tabulated results.

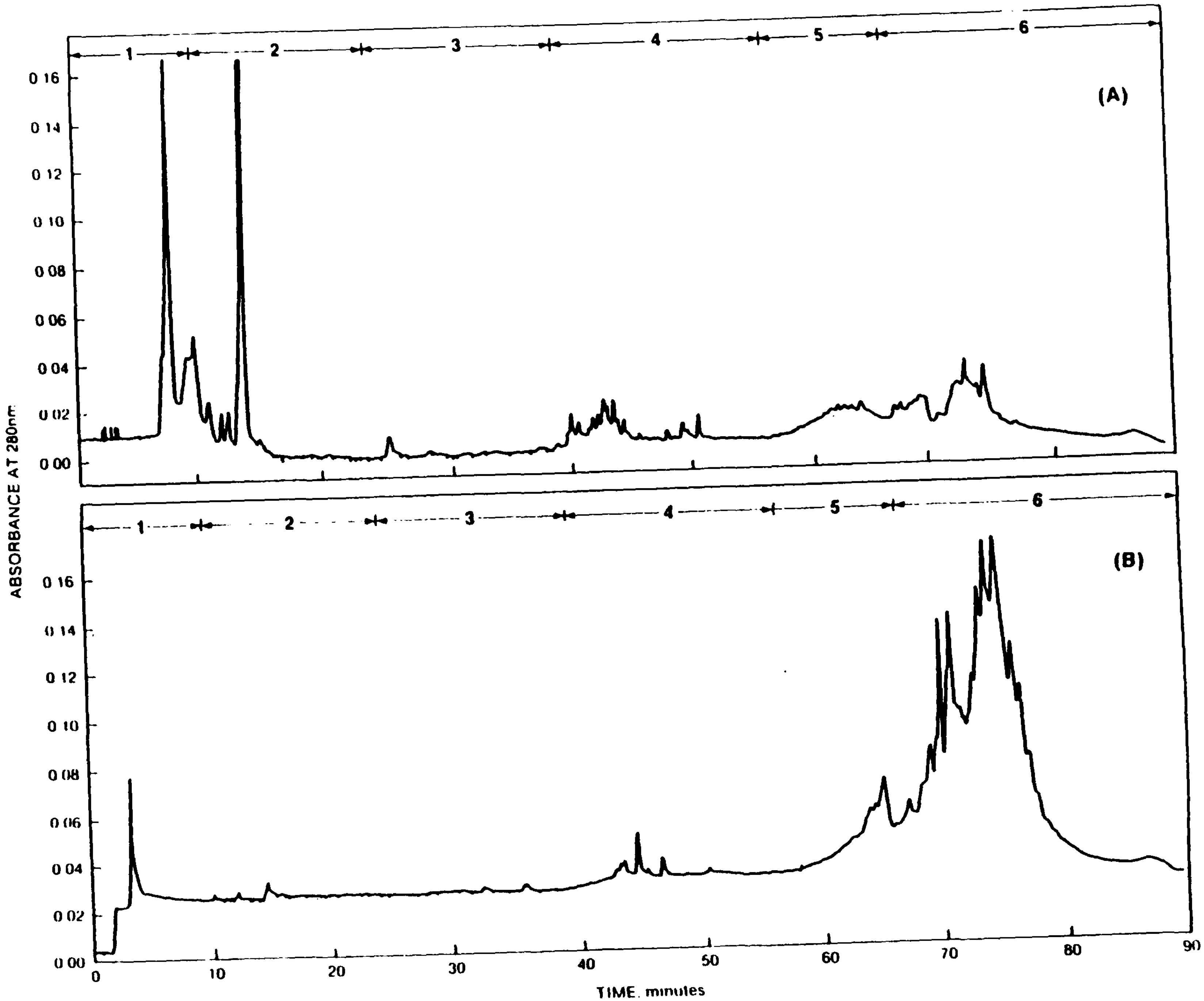

FIGURE 3. - HPLC chromatograms from subfractionation of fuel 2987 whole acid (A) and fuel 2987 sediment (B).

Because of the limited amounts of filterable sediments and the brittle nature of the filters used with the JFTOT apparatus (nylon for fuel 2987 and glass fiber for fuel 2955), the sediments could not be sampled by scraping them from the filter surface. However, they were sampled successfully by cutting small filter strips to be placed in the probe for introduction into the mass spectrometer. Using this approach, spectra of the sediments were recorded under the same conditions as given for the tube deposits, except that 25 eV electron impact was used for ionization of the sediment from fuel 2955. The lower-energy ionization was selected to suppress intensities of fragment-ion peaks, but this method did not appear to offer any advantage over 70 eV electron impact and was not used with the other samples. To avoid thermal decomposition of the nylon filter used in the JFTOT apparatus during experiments with fuel 2987, probe temperature was limited to approximately 300° C when mass spectra of the sediment on the filter were recorded.

Presentation of Results. To make a reasonable comparison in a limited amount of space of results obtained from a large amount of mass-spectral data, abbreviation in tabulated form is used to discuss the compound types identified in the solids formed during fuel degradation. Each table presents ions detected in homologous series corresponding to a particular elemental composition. For example, ions arising from hydrocarbons are classified as having C_nH_{2n+z} compositions where z ranges from +2 to -23. Thus, molecular ions for alkylbenzenes (C_nH_{2n-6}) are listed under a z number of -6. Major fragment ions are given along with molecular ions. These occur in series having a z number one less than the number for molecular ions. For alkylbenzenes, fragment ions thus occur in the C_nH_{2n-7} series (z number of -7). No ion intensities are given, but the prominence of homologues in a particular series can be estimated from the number of molecular and fragment ions detected for the series. The molecular mass of the first member of a series is identified with the parent compound, e.g., 78 with benzene in the alkylbenzene series. If the first ion detected in a molecular-ion series has a mass less than the mass listed for the parent compound, the ion may arise by rearrangement or it may belong to a series for another type not identified. In either case, the fact that the ion cannot be a molecular ion in the listed series is mentioned in a footnote to the table.

It is necessary to emphasize that names of compound types given in the first column of the tables are intended to be suggestions only. Undoubtedly, many of the ions having the specified elemental composition do arise from the type indicated; however, others may originate from types not identified. In the discussion that follows, names are restricted to those given in the tables with the understanding that ions in the series can originate from other compound types as well.

Analysis of Filterable Sediment and Tube Deposit from Fuel 2987. Numerous compound types were detected in the solids formed during thermal stressing of the jet fuel from coal, including those containing only carbon and hydrogen as well as heteroatomic types containing oxygen and nitrogen. No more than traces of compounds containing sulfur were found.

In tables 10 and 11, respectively, identification of hydrocarbons in the filterable sediment and tube deposit is presented for the thermal degradation of fuel 2987. A broad range of aliphatic and alicyclic compound types was found in both solids. No molecular ions for alkanes were identified (nor were they expected), but fragment ions corresponding to alkyl groups were found over a mass range extending to m/z 155 in the spectra from the sediment and to m/z 183 in the spectra from the tube deposit. These fragments may arise from alkanes or from other compound types having alkyl side chains. Numerous molecular and fragment ions were recorded for olefins and cycloalkanes. These compound types are distributed rather uniformly between the tube deposit and the filterable sediment. For example, molecular ions for dienes, cycloalkenes, and bicycloalkanes were detected from m/z 68 to m/z 194 in the spectra from both solids. The ions appear in the spectra over a broad range of probe temperatures, indicating that they arise from surface desorption and by covalent bond rupture, i.e., by pyrolysis.

Many molecular and fragment ions from aromatic hydrocarbons were detected in the spectra from the filterable sediment and tube deposit. Alkylbenzene homologues were identified in the sediment to 190 amu and in the tube deposit to 162 amu. Indans and tetralins were found in both solids with molecular masses extending to 188 amu. Aromatics with a greater degree of unsaturation were evident in both sets of spectra. Six members of the naphthalene series (z number of -12) were identified in the sediment spectra and five members in the spectra from the tube deposit. The most highly aromatic types identified in either set of spectra were the fluoranthenes and pyrenes (z number of -22). One member of the series, the parent compound at m/z 202, was identified in the spectra of the sediment, and three members (m/z 202, 216, and 244) were found in the tube-deposit spectra.

A number of molecular and fragment ions containing one oxygen were identified in the spectra from the filterable sediment and tube deposit. These are seen in tables 12 and 13, respectively. Molecular ions for aliphatic and alicyclic types (e.g., tetrahydrofurans) were almost nonexistent in the spectra, and they were not expected based on the known fragmentation of these types of compounds. However, a number of fragment ions for aliphatics and alicyclics were detected, as noted in the tables.

Aromatics containing one oxygen were readily detected in both sets of spectra. Several phenols were identified, as well as a number of more unsaturated types, including naphthols and dibenzofurans. Compounds with a greater degree of unsaturation appeared to be partitioned more toward the filterable sediment than toward the tube deposit. As an illustration, four fluorenones (parent mass of 180) were detected in the sediment, but none were found in the tube deposit.

Table 10. - Mass-spectrometric analysis of filterable sediment from thermally stressed fuel 2987. Identification of hydrocarbons.

Suggested Origin[1]	Elemental Composition: C_nH_{2n+z}	Homologous Ions Detected
	z = +2	---
	+1	71-155
Olefins, cycloalkanes (70)	0	70-140[2]
	-1	69-167
Dienes, cycloalkenes (68), bicycloalkanes	-2	68-194
	-3	81-207
Cyclic dienes (66), tricycloalkanes	-4	80-178
	-5	79-191
Alkylbenzenes (78)	-6	92, 106, 134, 148, 176, 190
	-7	77-189
Indans (118), tetralins	-8	76-188[3]
	-9	75-173
Indenes (116), dihydronaphthalenes	-10	74-200[3]
	-11	73-157
Naphthalenes (128)	-12	114-142, 170-212[3]
	-13	113-211
Acenaphthenes (154), biphenyls	-14	126, 154[3]
	-15	125-195
Acenaphthylenes (152), biphenylenes, fluorenes	-16	152-194[3]
	-17	151-193
Anthracenes (178), phenanthrenes	-18	150-206[3]
	-19	163, 191, 205
Methylenephenanthrenes (190), phenylnaphthalenes	-20	176, 190[3]
	-21	189, 203
Fluoranthenes, pyrenes (202)	-22	202
	-23	215

[1]Molecular mass of first member of homologous series in parentheses.
[2]Series may contain rearrangement ions.
[3]First members of series may represent rearrangement ions.

Table 11. - Mass-spectrometric analysis of JFTOT tube deposit from thermally stressed fuel 2987. Identification of hydrocarbons.

Suggested Origin[1]	Elemental Composition: C_nH_{2n+z}	Homologous Ions Detected
	z = +2	---
	+1	71-183
Olefins, cycloalkanes (70)	0	70-140, 168[2]
	-1	69-153
Dienes, cycloalkenes (68),	-2	68-194
bicycloalkanes	-3	81-179
Cyclic dienes (66),	-4	80-192
tricycloalkanes	-5	79-205
Alkylbenzenes (78)	-6	78-162
	-7	77-203
Indans (118), tetralins	-8	76-188[3]
	-9	75-187
Indenes (116),	-10	74-186[3],
dihydronaphthalenes	-11	87-185, 213
Naphthalenes (128)	-12	114-184[3]
	-13	113-197
Acenaphthenes (154),	-14	126, 154-196[3]
biphenyls	-15	139-195
Acenaphthylenes (152),	-16	152-208
biphenylenes, fluorenes	-17	151-207
Anthracenes (178),	-18	164-220[3]
phenanthrenes	-19	163-205
Methylenephenanthrenes (190),	-20	176, 204, 218[3]
phenylnaphthalenes	-21	133, 189-217
Fluoranthenes, pyrenes (202)	-22	202, 216, 244
	-23	145, 215, 229

[1]Molecular mass of first member of homologous series in parentheses.
[2]Series may contain rearrangement ions.
[3]First members of series may represent rearrangement ions.

Table 12. - Mass-spectrometric analysis of filterable sediment from thermally stressed fuel 2987. Identification of compounds containing one oxygen.

Suggested Origin[1]	Elemental Composition: $C_nH_{2n+z}O$	Homologous Ions Detected
	z = +2	---
	+1	73
Tetrahydrofurans (72)	0	---
	-1	71-113, 239
Dihydrofurans (70)	-2	70-112
	-3	69-139
Furans (68)	-4	68-110, 138
	-5	81-151
Phenols (94)	-6	94-150
	-7	93-163, 191
Dihydrobenzofurans (120), hydroxyindans	-8	120-162
	-9	105-175
Benzofurans (118), indanones	-10	104-188[2]
	-11	131-201
Naphthols (144)	-12	130-214[2]
	-13	143-199
Acenaphthenols (170)	-14	156-226[2]
	-15	155-211, 253
Dibenzofurans (168)	-16	168-210
	-17	181-209
Fluorenones (180)	-18	180-222
	-19	207
	...	...
	-22	218, 246

[1]Molecular mass of first member of homologous series in parentheses.
[2]First member of series may represent rearrangement ion.

Table 13. - Mass-spectrometric analysis of JFTOT tube deposit from thermally stressed fuel 2987. Identification of compounds containing one oxygen.

Suggested Origin[1]	Elemental Composition: $C_nH_{2n+z}O$	Homologous Ions Detected
	z = +2	---
	+1	---
Tetrahydrofurans (72)	0	72
	-1	71-127
Dihydrofurans (70)	-2	70-126
	-3	69-139
Furans (68)	-4	68-152
	-5	81-165
Phenols (94)	-6	94-122
	-7	107-135
Dihydrobenzofurans (120),	-8	106-162[2]
hydroxyindans	-9	105-161
Benzofurans (118),	-10	104-188[2]
indanones	-11	131-173
Naphthols (144)	-12	144-200
	-13	157-185
Acenaphthenols (170)	-14	184, 198
	-15	155-197
Dibenzofurans (168)	-16	182, 196
	-17	181-209
Fluorenones (180)	-18	---
	-19	---

[1]Molecular mass of first member of homologous series in parentheses.
[2]First member of series may represent rearrangement ion.

Compound types containing two oxygens were identified in the spectra of the filterable sediment and tube deposit, including nonaromatic and aromatic carboxylic acids and dihydroxyaromatics. These are shown in tables 14 and 15. The aromatics are decidedly partitioned more toward the sediment. For example, six benzoic acids and benzodioxoles were found in the spectra of the sediment ranging from the parent compound (m/z 122) to homologues having five alkyl carbons attached (m/z 192). On the other hand, in the spectra of the tube deposit only one fragment ion attributable to these compound types was detected (m/z 149). Although molecular ions containing two oxygens were detected in z series as negative as -18 in the spectra of the sediment, no molecular ions in series more negative than -4 were detected in the tube-deposit spectra.

Tables 16 and 17 show ions detected in homologous series corresponding to compounds containing three oxygens. Because of the more complex nature of these types, names are omitted except to note that ions in the -2 and -3 z series are attributed to "multifunctional compounds" and that phthalates are indicated by fragment rearrangement ions in the -10 and -11 z series, particularly by the ion at m/z 149. Phthalates, especially dioctylphthalate, are common artifacts seen in mass spectra, and no further discussion of this type is warranted.

A very prominent peak appears in the spectra of the tube deposit at m/z 129, corresponding to a fragment ion of elemental composition $C_6H_9O_3$. It must arise from a nonaromatic oxygen-containing compound, such as an alcohol, ether, or peroxide. None of these compound types would produce a significant molecular ion. At first glance, m/z 129 might appear to have an elemental composition of C_9H_7N, corresponding to quinoline or isoquinoline. However, the accurately measured mass of the peak is consistently closer to the value expected for the CHO_3 combination (129.0552) than for the CHN combination (129.0578). Therefore, a composition of C_9H_7N is ruled out. The $C_6H_9O_3$ ion at m/z 129 is much smaller in the spectra of the filterable sediment, showing that the corresponding compound(s) is strongly partitioned toward the tube deposit.

Except for the compound(s) producing the m/z 129 peak, types containing three oxygens are partitioned more toward the sediment than toward the tube deposit. This is evident from the larger number of molecular and fragment ions seen in table 16 as compared with the number appearing in table 17. This difference is not easily explainable, but it may result from the relatively low thermal stability of compounds containing alcohol or ether groups; that is, these compounds may appear in smaller quantities in the tube deposit because they have been thermally decomposed on the hot metallic surface of the tube.

A number of compounds containing one nitrogen were identified in the filterable sediment, but only a few were found in the tube deposit, as seen by comparing results in tables 18 and 19. The difference may be a consequence of thermal decomposition of nitrogenous compounds on the hot tube surface. Compound types prominent in the spectra of the filterable sediment include pyrrolines (molecular ions from m/z 69 to 125 and 153) and aromatic types such as pyridines (or anilines), showing molecular ions from m/z 79 to m/z 149. Indolines, indoles, and quinolines (or isoquinolines) are abundant, as indicated by the number of molecular and fragment ions detected in homologous series for these types.

Table 14. - Mass-spectrometric analysis of filterable sediment from thermally stressed fuel 2987. Identification of compounds containing two oxygens.

Suggested Origin[1]	Elemental Composition: $C_nH_{2n+z}O$	Homologous Ions Detected
	z = +2	---
	+1	257
Aliphatic carboxylic acids,	0	74, 256
esters	-1	73-129, 157, 185, 213
Alicyclic carboxylic	-2	100, 114
acids (86), esters	-3	85-113
Hydroxyfurans, furanones (84)	-4	112
	-5	97, 111
Dihydroxybenzenes (110)	-6	110-152
	-7	123-151
Benzoic acids (122),	-8	122-192
benzodioxoles	-9	121-191
Hydroxybenzofurans (134),	-10	134-218
coumaranones	-11	133-203
Coumarins (146),	-12	146-216
dihydroxynaphthalenes	-13	159-201
Naphthoic acids (172),	-14	172-214
biphenols	-15	171-213
Hydroxydibenzofurans (184)	-16	184-212
	-17	197, 211
Biphenylene carboxylic acids	-18	196, 210
(196), hydroxyfluorenones	-19	---

[1]Molecular mass of first member of homologous series in parentheses.

Table 15. - Mass-spectrometric analysis of JFTOT tube deposit from thermally stressed fuel 2987. Identification of compounds containing two oxygens.

Suggested Origin[1]	Elemental Composition: $C_nH_{2n+z}O_2$	Homologous Ions Detected
	z = +2	---
	+1	229, 257
Aliphatic carboxylic acids,	0	74, 102, 116, 256
esters	-1	73-227, 255
Alicyclic carboxylic	-2	100, 114, 212
acids (86), esters	-3	85-127
Hydroxyfurans, furanones (84)	-4	98, 112, 154
	-5	111
Dihydroxybenzenes (110)	-6	---
	-7	95-123[2]
Benzoic acids (122),	-8	---
benzodioxoles	-9	149
Hydroxybenzofurans (134),	-10	---
coumaranones	-11	147
Coumarins (146),	-12	---
dihydroxynaphthalenes	-13	---
Naphthoic acids (172),	-14	---
biphenols	-15	---
Hydroxydibenzofurans (184)	-16	---
	-17	---
Biphenylene carboxylic acids	-18	---
(196), hydroxyfluorenones	-19	---

[1] Molecular mass of first member of homologous series in parentheses.
[2] Ion at m/z 95 probably originates from different molecular structure.

Table 16. - Mass-spectrometric analysis of filterable sediment from thermally stressed fuel 2987. Identification of compounds containing three oxygens.[1]

Suggested Origin	Elemental Composition: $C_nH_{2n+z}O_3$	Homologous Ions Detected
	z = +2	78, 162
	+1	119-147
	0	104, 146-174
	-1	131, 145
Multifunctional compounds	-2	116-172
	-3	129, 157
	-4	100, 128, 170
	-5	141-183
	-6	154, 182
	-7	167, 181
	-8	166, 208, 222
	-9	221, 235
Phthalates	-10	150-178, 220
	-11	149-191

[1]Peaks overlap with those containing one nitrogen.

Table 17. - Mass-spectrometric analysis of JFTOT tube deposit from thermally stressed fuel 2987. Identification of compounds containing three oxygens.[1]

Suggested Origin	Elemental Composition: $C_nH_{2n+z}O_3$	Homologous Ions Detected
	z = +2	---
	+1	---
	0	---
	-1	---
Multifunctional compounds	-2	242
	-3	129[2], 143, 185, 241
	-4	100, 128, 142
	-5	127
	-6	---
	-7	---
	-8	152
	-9	151
Phthalates	-10	---
	-11	149

[1]Peaks overlap with those containing one nitrogen.
[2]Very strong peak at m/z 129.

Table 18. - Mass-spectrometric analysis of filterable sediment from thermally stressed fuel 2987. Identification of compounds containing one nitrogen.[1]

Suggested Origin[2]	Elemental Composition: $C_nH_{2n+z}N$	Homologous Ions Detected
Aliphatic amines	z = +3	---
	+2	72-100
Pyrrolidines (71), piperidines	+1	85
	0	70-112
Pyrrolines (69)	-1	69-125, 153
	-2	68-152
Pyrroles (67)	-3	81, 95, 123
	-4	80-150
Pyridines (79), anilines	-5	79-149
	-6	78-162
Indolines (119)	-7	91-175[3]
	-8	76-174
Indoles (117)	-9	75, 103-173[3]
	-10	88-158, 228
Quinolines (129), isoquinolines	-11	129-171
	-12	114-184
Phenylpyridines (155)	-13	127-183[3]
	-14	140-196
Carbazoles (167)	-15	153-181[3]
	-16	152, 194, 208
Acridines (179), phenanthridines	-17	179, 193, 221
	-18	178, 220
	-19	163-191
	-20	162-204, 232
Aminofluoranthenes (217), aminopyrenes	-21	217
	-22	188, 216-244

[1] Peaks overlap with those containing three oxygens.
[2] Molecular mass of first member of homologous series in parentheses.
[3] First members of series may represent rearrangement ions.

Table 19. - Mass-spectrometric analysis of JFTOT tube deposit from thermally stressed fuel 2987. Identification of compounds containing one nitrogen.[1]

Suggested Origin[2]	Elemental Composition: $C_nH_{2n+z}N$	Homologous Ions Detected
Aliphatic amines	z = +3	---
	+2	268, 296[3]
Pyrrolidines (71), piperidines	+1	---
	0	294[3]
Pyrrolines (69)	-1	---
	-2	---
Pyrroles (67)	-3	---
	-4	---
Pyridines (79), anilines	-5	---
	-6	---
Indolines (119)	-7	---
	-8	---
Indoles (117)	-9	---
	-10	242[3]
Quinolines (129), isoquinolines	-11	185, 241[3]
	-12	---
Phenylpyridines (155)	-13	---
	-14	---
Carbazoles (167)	-15	---
	-16	---
Acridines (179), phenanthridines	-17	---
	-18	---
	-19	---
	-20	---
Aminofluoranthenes (217), aminopyrenes	-21	---
	-22	---

[1]Peaks overlap with those containing three oxygens.
[2]Molecular mass of first member of homologous series in parentheses.
[3]Ions probably originate from different molecular structure.

Analysis of Filterable Sediment and Tube Deposit from Fuel 2955. In spite of the different origins of fuel 2987 (coal liquid) and fuel 2955 (petroleum), mass-spectral analyses of solids formed by thermally stressing the two fuels produced surprisingly similar results. Therefore, discussion of the compositions of the filterable sediment and tube deposit from fuel 2955 will be limited mainly to differences found between the solids formed from the two fuels.

Tables 20 and 21 show the identification of hydrocarbons in the filterable sediment and tube deposit from fuel 2955. When these results are compared with those in tables 10 and 11 for fuel 2987, it becomes evident that the compositions of the hydrocarbons in the solids from the two fuels are very similar. This observation suggests that the same hydrocarbons are contributing to the formation of the solids in both fuels.

Compound types identified as having one oxygen in the filterable sediment and tube deposit from fuel 2955 are given in tables 22 and 23, respectively. When compared with the same types identified in the solids from fuel 2987 (tables 12 and 13), only slight differences are seen that may not be significant. For example, only one dibenzofuran (mass 196) was detected in the sediment from fuel 2955, but in the sediment from fuel 2987 four homologues were found (masses 168 to 210). Several fluorenones were detected in the tube deposit from fuel 2955 but not in the sediment from the same fuel. The opposite was found for fuel 2987, i.e., fluorenones were detected in the sediment but not in the tube deposit.

Fewer compounds containing two oxygens were found in the filterable sediment from fuel 2955 than in the sediment from fuel 2987. This is seen by comparing results in table 24 with those in table 14. Differences are particularly evident for the more unsaturated species. No types with z numbers more negative than -12 (coumarins and dihydroxynaphthalenes) were detected in the fuel 2955 sediment, whereas, in the sediment from fuel 2987 types with z numbers as negative as -18 were identified (biphenylene carboxylic acids and hydroxyfluorenones). In contrast, by comparing results in tables 25 and 15, it is evident that more types containing two oxygens, especially aromatics, were detected in the tube deposit from fuel 2955 than in the 2987 deposit.

A very similar distribution of compound types containing three oxygens was found between the filterable sediments from the two fuels as well as between their tube deposits. Compare results in tables 26 and 27 with those in tables 16 and 17. As mentioned previously, a very strong m/z 129 peak of elemental composition $C_6H_9O_3$ was found in the spectra of the tube deposit from fuel 2987 (table 17). This same peak was present in the spectra of the 2955 tube deposit (table 27) although its intensity was not as strong as in the 2987 spectra. The $C_6H_9O_3$ ion was also detected in the spectra of the filterable sediment from fuel 2955; however, its intensity was much weaker than in the spectra of the tube deposit from the same fuel (table 26 vs. table 27).

Table 20. - Mass-spectrometric analysis of filterable sediment from thermally stressed fuel 2955. Identification of hydrocarbons.

Suggested Origin[1]	Elemental Composition: C_nH_{2n+z}	Homologous Ions Detected
	z = +2	---
	+1	71-113
Olefins, cycloalkanes (70)	0	84-112[2]
	-1	83-139
Dienes, cycloalkenes (68),	-2	82-124, 152
bicycloalkanes	-3	81-137
Cyclic dienes (66),	-4	80-108
tricycloalkanes	-5	79-149
Alkylbenzenes (78)	-6	92, 120[3]
	-7	77, 105-147[3]
Indans (118), tetralins	-8	76-132[4]
	-9	75-145
Indenes (116),	-10	74, 102-144[4]
dihydronaphthalenes	-11	101-157
Naphthalenes (128)	-12	128-170
	-13	127-169
Acenaphthenes (154),	-14	126[4]
biphenyls	-15	139-167
Acenaphthylenes (152),	-16	152-180
biphenylenes, fluorenes	-17	165-193
Anthracenes (178),	-18	178-206
phenanthrenes	-19	191
Methylenephenanthrenes (190),	-20	176[4]
phenylnaphthalenes	-21	---
Fluoranthenes, pyrenes (202)	-22	---
	-23	215

[1]Molecular mass of first member of homologous series in parentheses.
[2]Series may contain rearrangement ions.
[3]Peaks at m/z 106 and 91 used as reference in 25 eV spectrum (omitted from table).
[4]First members of series may represent rearrangement ions.

Table 21. - Mass-spectrometric analysis of JFTOT tube deposit from thermally stressed fuel 2955. Identification of hydrocarbons.

Suggested Origin[1]	Elemental Composition: C_nH_{2n+z}	Homologous Ions Detected
	z = +2	---
	+1	71-183
Olefins, cycloalkanes (70)	0	70-168[2]
	-1	69-167
Dienes, cycloalkenes (68), bicycloalkanes	-2	68-194
	-3	81-193
Cyclic dienes (66), tricycloalkanes	-4	80-150, 192
	-5	79-191
Alkylbenzenes (78)	-6	78-162
	-7	77-161
Indans (118), tetralins	-8	76-146[3]
	-9	75-173
Indenes (116), dihydronaphthalenes	-10	74-116, 144[3]
	-11	87-171
Naphthalenes (128)	-12	114-184[3]
	-13	113-183
Acenaphthenes (154), biphenyls	-14	126-182[3]
	-15	139-181
Acenaphthylenes (152), biphenylenes, fluorenes	-16	152-180
	-17	151-193
Anthracenes (178), phenanthrenes	-18	178-206
	-19	163-191
Methylenephenanthrenes (190), phenylnaphthalenes	-20	176[3]
	-21	133-161, 189
Fluoranthenes, pyrenes (202)	-22	202
	-23	145

[1]Molecular mass of first member of homologous series in parentheses.
[2]Series may contain rearrangement ions.
[3]First members of series may represent rearrangement ions.

Table 22. - Mass-spectrometric analysis of filterable sediment from thermally stressed fuel 2955. Identification of compounds containing one oxygen.

Suggested Origin[1]	Elemental Composition: $C_nH_{2n+z}O$	Homologous Ions Detected
	z = +2	---
	+1	---
Tetrahydrofurans (72)	0	---
	-1	71, 85
Dihydrofurans (70)	-2	84-112
	-3	83-111
Furans (68)	-4	82-110
	-5	95-123
Phenols (94)	-6	94-150
	-7	107-149
Dihydrobenzofurans (120),	-8	120-162
hydroxyindans	-9	105-161
Benzofurans (118),	-10	132-174
indanones	-11	131-173
Naphthols (144)	-12	144-186
	-13	157, 171
Acenaphthenols (170)	-14	184
	-15	155-183
Dibenzofurans (168)	-16	196
	-17	181
Fluorenones (180)	-18	---
	-19	---

[1]Molecular mass of first member of homologous series in parentheses.

Table 23. - Mass-spectrometric analysis of JFTOT tube deposit from thermally stressed fuel 2955. Identification of compounds containing one oxygen.

Suggested Origin[1]	Elemental Composition: $C_nH_{2n+z}O$	Homologous Ions Detected
	z = +2	---
	+1	73, 87
Tetrahydrofurans (72)	0	72
	-1	71-99, 127
Dihydrofurans (70)	-2	70-112
	-3	69-153
Furans (68)	-4	68-152
	-5	81-165
Phenols (94)	-6	94, 122, 136
	-7	93-135
Dihydrobenzofurans (120), hydroxyindans	-8	120-148
	-9	105-161
Benzofurans (118), indanones	-10	104-160[2]
	-11	131-173
Naphthols (144)	-12	144-186
	-13	157-185
Acenaphthenols (170)	-14	170, 184
	-15	155-183
Dibenzofurans (168)	-16	182, 196
	-17	181, 209
Fluorenones (180)	-18	180-208
	-19	---

[1]Molecular mass of first member of homologous series in parentheses.
[2]First member of series may represent rearrangement ion.

Table 24. - Mass-spectrometric analysis of filterable sediment from thermally stressed fuel 2955. Identification of compounds containing two oxygens.

Suggested Origin[1]	Elemental Composition: $C_nH_{2n+z}O_2$	Homologous Ions Detected
	z = +2	76
	+1	---
Aliphatic carboxylic acids,	0	74, 256
esters	-1	73-185
Alicyclic carboxylic	-2	---
acids (86), esters	-3	85
Hydroxyfurans, furanones (84)	-4	98
	-5	---
Dihydroxybenzenes (110)	-6	124
	-7	---
Benzoic acids (122),	-8	136-164
benzodioxoles	-9	121-163
Hydroxybenzofurans (134),	-10	148-176
coumaranones	-11	161, 175
Coumarins (146),	-12	174-202
dihydroxynaphthalenes	-13	---
Naphthoic acids (172),	-14	---
biphenols	-15	---
Hydroxydibenzofurans (184)	-16	---
	-17	---
Biphenylene carboxylic acids	-18	---
(196), hydroxyfluorenones	-19	---

[1]Molecular mass of first member of homologous series in parentheses.

Table 25. - Mass-spectrometric analysis of JFTOT tube deposit from thermally stressed fuel 2955. Identification of compounds containing two oxygens.

Suggested Origin[1]	Elemental Composition: $C_nH_{2n+z}O_2$	Homologous Ions Detected
	z = +2	---
	+1	257
Aliphatic carboxylic acids, esters	0	74, 102, 116, 256, 284
	-1	73-227
Alicyclic carboxylic acids (86), esters	-2	86-114
	-3	85-127
Hydroxyfurans, furanones (84)	-4	98, 112
	-5	97, 111
Dihydroxybenzenes (110)	-6	82, 96, 124[2]
	-7	95-123
Benzoic acids (122), benzodioxoles	-8	122-164
	-9	121-163
Hydroxybenzofurans (134), coumaranones	-10	134-176
	-11	133-175
Coumarins (146), dihydroxynaphthalenes	-12	146-174
	-13	117, 159, 173
Naphthoic acids (172), biphenols	-14	172, 186
	-15	---
Hydroxydibenzofurans (184)	-16	---
	-17	---
Biphenylene carboxylic acids (196), hydroxyfluorenones	-18	---
	-19	---

[1]Molecular mass of first member of homologous series in parentheses.
[2]First members of series may represent rearrangement ions.

Table 26. - Mass-spectrometric analysis of filterable sediment from thermally stressed fuel 2955. Identification of compounds containing three oxygens.[1]

Suggested Origin	Elemental Composition: $C_nH_{2n+z}O_3$	Homologous Ions Detected
	z = +2	120-176
	+1	119-203
	0	118-216
	-1	117-229
Multifunctional compounds	-2	116-214
	-3	129-199
	-4	142-184
	-5	155, 169, 197
	-6	126-168, 196, 210
	-7	167-195
	-8	152, 166, 208
	-9	---
Phthalates	-10	178
	-11	149, 163
	-12	190, 204
	-13	---

[1]Peaks overlap with those containing one nitrogen.

Table 27. - Mass-spectrometric analysis of JFTOT tube deposit from thermally stressed fuel 2955. Identification of compounds containing three oxygens.[1]

Suggested Origin	Elemental Composition: $C_nH_{2n+z}O_3$	Homologous Ions Detected
	z = +2	---
	+1	---
	0	---
	-1	---
Multifunctional compounds	-2	116-144
	-3	129[2], 171, 185, 241
	-4	128, 142
	-5	---
	-6	---
	-7	---
	-8	152
	-9	151
Phthalates	-10	---
	-11	149, 163
	-12	162
	-13	---

[1]Peaks overlap with those containing one nitrogen.
[2]Strong peak at m/z 129.

Tables 28 and 29 show ions containing one nitrogen identified in the spectra of the filterable sediment and tube deposit, respectively, from fuel 2955. The corresponding compound types are seen to be distributed more toward the sediment than toward the tube deposit. This same observation was noted in the discussion above of the results from solids formed during thermal stressing of fuel 2987. Although the compositions with respect to nitrogen-containing compounds are similar in the sediments from the two fuels (table 28 vs. table 18), fewer highly aromatic types were detected in the spectra of the sediment from fuel 2955. For example, only one homologue for acridines and phenanthridines (mass 193) was identified in the 2955 spectra, but three were found in the spectra of the 2987 sediment (masses 179, 193, and 221). A few nitrogen-containing species were detected in the tube deposit from fuel 2955 as compared to virtually none in the spectra of the 2987 deposit (table 29 vs. table 19). In this respect, several quinolines (or isoquinolines) were identified in the tube deposit from fuel 2955, but the presence of this compound type in the 2987 deposit is in doubt, as noted in table 19.

Summary of Mass Spectral Results from the Analysis of Filterable Sediments and Tube Deposits. Mass spectra of the filterable sediments and JFTOT-tube deposits formed during thermal stressing of the coal-derived and petroleum-derived fuels are remarkably similar, indicating that the same compound types are responsible for solids formation in both fuels.

When spectra of the filterable sediment from either fuel are compared with those of the tube deposit from the same fuel, a number of similarities are found as well as some significant differences. Both sets of spectra show molecular- and fragment-ion peaks for aromatic and nonaromatic hydrocarbons and for compounds containing one to three oxygens. Strong peaks are observed in the spectra of the filterable sediment corresponding to aromatic compounds containing one nitrogen. These peaks are much weaker or absent in the spectra from the tube deposit. No spectra of the sediment or tube deposit from either fuel show any more than traces of sulfur-containing compounds.

An intense, nonaromatic fragment ion containing three oxygens was identified in the spectra of the tube deposits from both fuels. This ion was also found in the spectra of the filterable sediments from both fuels although its intensity was much weaker. The ion could not be correlated with a molecular ion from any particular compound type, but it may have originated from an alcohol, ether, or some other type that does not produce a significant molecular ion.

Although the structural information obtained through mass-spectral analysis of the filterable sediments and tube deposits has not specifically identified precursors responsible for solids formation in the two fuels, the results presented demonstrate the potential of the method for studying the mechanisms leading to fuel degradation under conditions of high temperature, such as those encountered in turbine engines.

Table 28. - Mass-spectrometric analysis of filterable sediment from thermally stressed fuel 2955. Identification of compounds containing one nitrogen.[1]

Suggested Origin[2]	Elemental Composition: $C_nH_{2n+z}N$	Homologous Ions Detected
Aliphatic amines	z = +3	---
	+2	86, 114
Pyrrolidines (71), piperidines	+1	---
	0	84, 112
Pyrrolines (69)	-1	---
	-2	82, 110
Pyrroles (67)	-3	---
	-4	80, 94
Pyridines (79), anilines	-5	93-177
	-6	92-176
Indolines (119)	-7	105-203[3]
	-8	104-216
Indoles (117)	-9	117-215
	-10	116-214
Quinolines (129), isoquinolines	-11	129-199
	-12	128-212
Phenylpyridines (155)	-13	155-197
	-14	140-210
Carbazoles (167)	-15	167-209
	-16	180-208
Acridines (179), phenanthridines	-17	193
	-18	---
	-19	---
	-20	190, 204
Aminofluoranthenes (217), aminopyrenes	-21	---
	-22	---

[1]Peaks overlap with those containing three oxygens.
[2]Molecular mass of first member of homologous series in parentheses.
[3]First members of series may represent rearrangement ions.

Table 29. - Mass-spectrometric analysis of JFTOT tube deposit from thermally stressed fuel 2955. Identification of compounds containing one nitrogen.[1]

Suggested Origin[2]	Elemental Composition: $C_nH_{2n+z}N$	Homologous Ions Detected
Aliphatic amines	z = +3	297[3]
	+2	296
Pyrrolidines (71), piperidines	+1	---
	0	70, 84
Pyrrolines (69)	-1	---
	-2	68
Pyrroles (67)	-3	---
	-4	---
Pyridines (79), anilines	-5	---
	-6	106, 120
Indolines (119)	-7	---
	-8	---
Indoles (117)	-9	---
	-10	144
Quinolines (129), isoquinolines	-11	129-185
	-12	128, 142
Phenylpyridines (155)	-13	---
	-14	---
Carbazoles (167)	-15	---
	-16	152
Acridines (179), phenanthridines	-17	151[3]
	-18	---
	-19	149, 163
	-20	162
Aminofluoranthenes (217), aminopyrenes	-21	---
	-22	---

[1]Peaks overlap with those containing three oxygens.
[2]Molecular mass of first member of homologous series in parentheses.
[3]Ions probably originate from different molecular structure.

Task 5. Liquid Fuel Analyses

Samples of the two JP-8 fuels (NIPER Nos. 2955 and 2987) were analyzed by high-resolution mass spectrometry before and after being subjected to the storage, thermal, and oxidation stability tests reported under Tasks 2 and 3 above.

Altogether, eight samples were analyzed, four from fuel 2955 and four from 2987. Each set of samples contained: (a) the fresh fuel; (b) fuel from the JFTOT thermal stability test (ASTM D 3241); (c) fuel from 4-week storage at 80° C; and (d) fuel from the oxidation stability test (ASTM D 2274).

All samples were analyzed in a Kratos MS-50 high resolution mass spectrometer (Kratos Analytical Instruments) with sample introduction through an all-glass expansion volume inlet (R. J. Brunfeldt Co.) operated at 300° C. The ion source temperature was 250° C. Seventy eV electron impact was used for ion formation, and masses were separated at a dynamic resolving power of at least 18,000. Ten or more spectra from one sample load were recorded at a scan rate of 100 seconds/decade.

The mass-spectral data were analyzed with a 22-component hydrocarbon type analysis program which provides a quantitative analysis for paraffins, cycloparaffins, aromatics, and sulfur-containing compounds (9,10).

Typical results from the analysis of the petroleum-derived fuel samples are given in tables 30-33. The fresh fuel sample and those from the stability tests all have virtually the same compositions with each consisting of 83-85 vol. % saturated hydrocarbons, 15-17 vol. % aromatic hydrocarbons, and less than 1 vol. % aromatic sulfur-containing compounds. These results show that only minor changes occurred in the composition of fuel 2955 during stability testing.

Tables 34-37 show typical results for the coal-liquid fuel samples. No significant differences in the compositions occurred during stability testing. However, when compared to the compositions of the petroleum-derived fuel samples, quite significant differences are evident. The coal-liquid fuel samples contain only 4-6 vol. % paraffins as compared to 42-43 vol. % paraffins in the petroleum-derived samples. In another significant difference, the coal-liquid samples contain 41-44 vol. % monocycloparaffins as compared to 28-30 vol. % monocycloparaffins in the petroleum-derived samples. Alkylbenzene levels were similar in the coal-liquid and petroleum-derived samples (12 vol. %) while hydroaromatics (benzocycloparaffins, z = -8) were more prevalent in the coal liquid (7-11 vs. 1-2 vol. %). No aromatic sulfur-containing compounds were detected in the coal-liquid samples although small quantities were found in the petroleum-derived samples. Other differences in the compositions of the fuels from the two sources are also evident.

In summary, the 22-component hydrocarbon type analysis did not detect any significant differences in the composition of either fuel upon stability testing. On the other hand, very significant differences were evident in the compositions of the petroleum-derived fuel and the coal-liquid fuel when one was compared to the other.

TABLE 30. Analysis of fresh petroleum-derived fuel 2955 by 22-component hydrocarbon type method

ANALYTICAL DIVISION
MASS SPECTROMETRY LABORATORY

PROGRAM 34 CALC. AT 15:17:54 ON 6/21/89
CUSTOMER: WH ACCT NO: 806817

RUN: 05159D. ACQU. AT 00:00:0 ON 5/15/89.
SAMPLE: 05159D9. 5/15/89. ANAL. OF FRESH FUEL 2955 BY HC22

C(N)H(2N+2)	PARAFFINS	43.3	
C(N)H(2N)	MONOCYCLOPARAFFINS	27.8	
C(N)H(2N-2)	DICYCLOPARAFFINS	11.6	
C(N)H(2N-4)	TRICYCLOPARAFFINS	1.9	
C(N)H(2N-6)	TETRACYCLOPARAFFINS	.0	
C(N)H(2N-8)	PENTACYCLOPARAFFINS	.0	
C(N)H(2N-10)	HEXACYCLOPARAFFINS	.0	
C(N)H(2N-12)	HEPTACYCLOPARAFFINS	.0	
	SATURATES		84.6
MONOAROMATICS			
C(N)H(2N)	ALKYLBENZENES	11.4	
C(N)H(2N-8)	BENZOCYCLOPARAFFINS	1.5	
C(N)H(2N-10)	BENZODICYCLOPARAFFINS	.0	
DIAROMATICS			
C(N)H(2N-12)	NAPHTHALENES	2.5	
C(N)H(2N-14)		.0	
C(N)H(2N-16)		.0	
TRIAROMATICS			
C(N)H(2N-18)		.0	
C(N)H(2N-22)		.0	
TETRAAROMATICS			
C(N)H(2N-24)		.0	
C(N)H(2N-28)		.0	
	AROMATICS		15.4
C(N)H(2N-4)S	THIOPHENES	.0	
C(N)H(2N-10)S	BENZOTHIOPENES	.0	
C(N)H(2N-16)S	DIBENZOTHIOPHENES	.0	
C(N)H(2N-22)S	NAPHTHOBENZOTHIOPHENES	.0	
	SULFUR COMPOUNDS		.0

CALCULATED %C= 85.9 %H= 14.1 %THIOPHENIC S= .00
AVERAGE C#= 12.6 AVERAGE MW= 172.8

PLEASE NOTE--
SAMPLE TYPES CORRECTLY ANALYZED
1. C12 TO C36, 250 DEG F TO 1050 DEG F HYDROCARBONS
2. OLEFIN-FREE HYDROCARBONS
3. LESS THAN 5% OXYGEN, NITROGEN, OR SULFUR COMPS.
ONLY LISTED TYPES ARE CONSIDERED, ALL OTHERS IGNORED

MATRIX COMPOSITION:

MTX	%	MTX	%	MTX	%	MTX	%
1	72.0	2	24.6	3	3.4	4	.0
5	.0	6	.0	7	.0	8	.0

Matrix selection based on distillation data

TABLE 31. Analysis of petroleum-derived fuel 2955 from JFTOT thermal stability test (ASTM D 3241) by 22-component hydrocarbon type method

ANALYTICAL DIVISION
MASS SPECTROMETRY LABORATORY

PROGRAM 34 CALC. AT 13:18:41 ON 6/23/89
CUSTOMER: WH ACCT NO: B06817

RUN: 05169B. ACQU. AT 00:00:0 ON 5/16/89.
SAMPLE: 0516989. 5/16/89. ANAL. OF STRESSED FUEL 2955 BY HC22

C(N)H(2N+2)	PARAFFINS	42.3	
C(N)H(2N)	MONOCYCLOPARAFFINS	30.2	
C(N)H(2N-2)	DICYCLOPARAFFINS	8.3	
C(N)H(2N-4)	TRICYCLOPARAFFINS	2.3	
C(N)H(2N-6)	TETRACYCLOPARAFFINS	.0	
C(N)H(2N-8)	PENTACYCLOPARAFFINS	.0	
C(N)H(2N-10)	HEXACYCLOPARAFFINS	.0	
C(N)H(2N-12)	HEPTACYCLOPARAFFINS	.0	
	SATURATES		83.1
MONOAROMATICS			
C(N)H(2N)	ALKYLBENZENES	11.9	
C(N)H(2N-8)	BENZOCYCLOPARAFFINS	1.5	
C(N)H(2N-10)	BENZODICYCLOPARAFFINS	.0	
DIAROMATICS			
C(N)H(2N-12)	NAPHTHALENES	3.4	
C(N)H(2N-14)		.1	
C(N)H(2N-16)		.0	
TRIAROMATICS			
C(N)H(2N-18)		.0	
C(N)H(2N-22)		.0	
TETRAAROMATICS			
C(N)H(2N-24)		.0	
C(N)H(2N-28)		.0	
	AROMATICS		16.9
C(N)H(2N-4)S	THIOPHENES	.0	
C(N)H(2N-10)S	BENZOTHIOPENES	.0	
C(N)H(2N-16)S	DIBENZOTHIOPHENES	.0	
C(N)H(2N-22)S	NAPHTHOBENZOTHIOPHENES	.0	
	SULFUR COMPOUNDS		.0

CALCULATED %C= 86.0 %H= 14.0 %THIOPHENIC S= .00
AVERAGE C#= 12.6 AVERAGE MW= 172.8

PLEASE NOTE--
SAMPLE TYPES CORRECTLY ANALYZED
1. C12 TO C36, 250 DEG F TO 1050 DEG F HYDROCARBONS
2. OLEFIN-FREE HYDROCARBONS
3. LESS THAN 5% OXYGEN, NITROGEN, OR SULFUR COMPS.
ONLY LISTED TYPES ARE CONSIDERED, ALL OTHERS IGNORED

MATRIX COMPOSITION:

MTX	%	MTX	%	MTX	%	MTX	%
1	72.0	2	24.6	3	3.4	4	.0
5	.0	6	.0	7	.0	8	.0

Matrix selection based on distillation data

TABLE 32. Analysis of petroleum-derived fuel 2955 aged four weeks at 80° C by 22-component hydrocarbon type method

ANALYTICAL DIVISION
MASS SPECTROMETRY LABORATORY

PROGRAM 34 CALC. AT 15:38: 8 ON 6/22/89
CUSTOMER: WH ACCT NO: BO6817

RUN: 051591. ACQU. AT 00:00:0 ON 5/15/89.
SAMPLE: 05159111. 5/15/89. ANAL. OF FUEL 2955-80-12, AGED 4 WKS, 80

C(N)H(2N+2)	PARAFFINS	42.4	
C(N)H(2N)	MONOCYCLOPARAFFINS	27.6	
C(N)H(2N-2)	DICYCLOPARAFFINS	10.1	
C(N)H(2N-4)	TRICYCLOPARAFFINS	2.6	
C(N)H(2N-6)	TETRACYCLOPARAFFINS	.0	
C(N)H(2N-8)	PENTACYCLOPARAFFINS	.0	
C(N)H(2N-10)	HEXACYCLOPARAFFINS	.0	
C(N)H(2N-12)	HEPTACYCLOPARAFFINS	.0	
	SATURATES		82.7
MONOAROMATICS			
C(N)H(2N)	ALKYLBENZENES	12.4	
C(N)H(2N-8)	BENZOCYCLOPARAFFINS	1.6	
C(N)H(2N-10)	BENZODICYCLOPARAFFINS	.0	
DIAROMATICS			
C(N)H(2N-12)	NAPHTHALENES	3.1	
C(N)H(2N-14)		.0	
C(N)H(2N-16)		.0	
TRIAROMATICS			
C(N)H(2N-18)		.0	
C(N)H(2N-22)		.0	
TETRAAROMATICS			
C(N)H(2N-24)		.0	
C(N)H(2N-28)		.0	
	AROMATICS		17.0
C(N)H(2N-4)S	THIOPHENES	.0	
C(N)H(2N-10)S	BENZOTHIOPENES	.3	
C(N)H(2N-16)S	DIBENZOTHIOPHENES	.0	
C(N)H(2N-22)S	NAPHTHOBENZOTHIOPHENES	.0	
	SULFUR COMPOUNDS		.3

CALCULATED %C= 85.9 %H= 14.0 %THIOPHENIC S= .05
AVERAGE C#= 12.6 AVERAGE MW= 173.1

PLEASE NOTE--
SAMPLE TYPES CORRECTLY ANALYZED
1. C12 TO C36, 250 DEG F TO 1050 DEG F HYDROCARBONS
2. OLEFIN-FREE HYDROCARBONS
3. LESS THAN 5% OXYGEN, NITROGEN, OR SULFUR COMPS.
ONLY LISTED TYPES ARE CONSIDERED, ALL OTHERS IGNORED

MATRIX COMPOSITION:

MTX	%	MTX	%	MTX	%	MTX	%
1	71.0	2	25.6	3	3.4	4	.0
5	.0	6	.0	7	.0	8	.0

Matrix selection based on distillation data

TABLE 33. Analysis of petroleum-derived fuel 2955 from oxidation stability test (ASTM D 2274) by 22-component hydrocarbon type method.

ANALYTICAL DIVISION
MASS SPECTROMETRY LABORATORY

PROGRAM 34 CALC. AT 12: 4:40 ON 6/27/89
CUSTOMER: WH ACCT NO: B06817

RUN: 05159C. ACQU. AT 00:00:0 ON 5/15/89.
SAMPLE: 05159C10. 5/15/89. FUEL 2955-4 FROM OX. STAB. TEST, 40 HRS

C(N)H(2N+2)	PARAFFINS	42.1	
C(N)H(2N)	MONOCYCLOPARAFFINS	29.9	
C(N)H(2N-2)	DICYCLOPARAFFINS	9.2	
C(N)H(2N-4)	TRICYCLOPARAFFINS	2.0	
C(N)H(2N-6)	TETRACYCLOPARAFFINS	.0	
C(N)H(2N-8)	PENTACYCLOPARAFFINS	.0	
C(N)H(2N-10)	HEXACYCLOPARAFFINS	.0	
C(N)H(2N-12)	HEPTACYCLOPARAFFINS	.0	
	SATURATES		83.2
MONOAROMATICS			
C(N)H(2N)	ALKYLBENZENES	12.1	
C(N)H(2N-8)	BENZOCYCLOPARAFFINS	2.0	
C(N)H(2N-10)	BENZODICYCLOPARAFFINS	.0	
DIAROMATICS			
C(N)H(2N-12)	NAPHTHALENES	2.2	
C(N)H(2N-14)		.1	
C(N)H(2N-16)		.0	
TRIAROMATICS			
C(N)H(2N-18)		.0	
C(N)H(2N-22)		.0	
TETRAAROMATICS			
C(N)H(2N-24)		.0	
C(N)H(2N-28)		.0	
	AROMATICS		16.4
C(N)H(2N-4)S	THIOPHENES	.0	
C(N)H(2N-10)S	BENZOTHIOPENES	.4	
C(N)H(2N-16)S	DIBENZOTHIOPHENES	.0	
C(N)H(2N-22)S	NAPHTHOBENZOTHIOPHENES	.0	
	SULFUR COMPOUNDS		.4

CALCULATED %C= 85.9 %H= 14.1 %THIOPHENIC S= .08
AVERAGE C#= 12.6 AVERAGE MW= 172.8

PLEASE NOTE--
SAMPLE TYPES CORRECTLY ANALYZED
1. C12 TO C36, 250 DEG F TO 1050 DEG F HYDROCARBONS
2. OLEFIN-FREE HYDROCARBONS
3. LESS THAN 5% OXYGEN, NITROGEN, OR SULFUR COMPS.
ONLY LISTED TYPES ARE CONSIDERED, ALL OTHERS IGNORED

MATRIX COMPOSITION:

MTX	%	MTX	%	MTX	%	MTX	%
1	72.0	2	24.6	3	3.4	4	.0
5	.0	6	.0	7	.0	8	.0

Matrix selection based on distillation data

TABLE 34. Analysis of fresh coal-liquid fuel 2987 by 22-component hydrocarbon type method

ANALYTICAL DIVISION
MASS SPECTROMETRY LABORATORY

PROGRAM 34 CALC. AT 16:38:18 ON 6/22/89
CUSTOMER: WH ACCT NO: B06817

RUN: 05169A. ACQU. AT 00:00:0 ON 5/16/89.
SAMPLE: 05169A9. 5/16/89. ANAL. OF FRESH FUEL 2987 BY HC22

C(N)H(2N+2)	PARAFFINS	5.2	
C(N)H(2N)	MONOCYCLOPARAFFINS	42.9	
C(N)H(2N-2)	DICYCLOPARAFFINS	19.8	
C(N)H(2N-4)	TRICYCLOPARAFFINS	8.8	
C(N)H(2N-6)	TETRACYCLOPARAFFINS	.0	
C(N)H(2N-8)	PENTACYCLOPARAFFINS	.0	
C(N)H(2N-10)	HEXACYCLOPARAFFINS	.0	
C(N)H(2N-12)	HEPTACYCLOPARAFFINS	.0	
	SATURATES		76.7
MONOAROMATICS			
C(N)H(2N)	ALKYLBENZENES	11.9	
C(N)H(2N-8)	BENZOCYCLOPARAFFINS	9.0	
C(N)H(2N-10)	BENZODICYCLOPARAFFINS	.9	
DIAROMATICS			
C(N)H(2N-12)	NAPHTHALENES	1.4	
C(N)H(2N-14)		.0	
C(N)H(2N-16)		.0	
TRIAROMATICS			
C(N)H(2N-18)		.0	
C(N)H(2N-22)		.0	
TETRAAROMATICS			
C(N)H(2N-24)		.0	
C(N)H(2N-28)		.0	
	AROMATICS		23.3
C(N)H(2N-4)S	THIOPHENES	.0	
C(N)H(2N-10)S	BENZOTHIOPENES	.0	
C(N)H(2N-16)S	DIBENZOTHIOPHENES	.0	
C(N)H(2N-22)S	NAPHTHOBENZOTHIOPHENES	.0	
	SULFUR COMPOUNDS		.0

CALCULATED %C= 86.8 %H= 13.2 %THIOPHENIC S= .00
AVERAGE C#= 12.6 AVERAGE MW= 173.1

PLEASE NOTE--
SAMPLE TYPES CORRECTLY ANALYZED
1. C12 TO C36, 250 DEG F TO 1050 DEG F HYDROCARBONS
2. OLEFIN-FREE HYDROCARBONS
3. LESS THAN 5% OXYGEN, NITROGEN, OR SULFUR COMPS.
ONLY LISTED TYPES ARE CONSIDERED, ALL OTHERS IGNORED

MATRIX COMPOSITION:

MTX	%	MTX	%	MTX	%	MTX	%
1	71.8	2	23.9	3	4.3	4	.0
5	.0	6	.0	7	.0	8	.0

Matrix selection based on distillation data

TABLE 35. Analysis of coal-liquid fuel 2987 from JFTOT thermal stability test (ASTM D 3241) by 22-component hydrocarbon type method

ANALYTICAL DIVISION
MASS SPECTROMETRY LABORATORY

PROGRAM 34 HC22_2 CALC. AT 12:15:43 ON 6/29/89
CUSTOMER: WH ACCT NO: B06817

RUN: 05169C. ACQU. AT 00:00:0 ON 5/16/89.
SAMPLE: 05169C9. 5/16/89. ANAL. OF STRESSED FUEL 2987 BY HC22

C(N)H(2N+2)	PARAFFINS	3.9	
C(N)H(2N)	MONOCYCLOPARAFFINS	41.6	
C(N)H(2N-2)	DICYCLOPARAFFINS	24.0	
C(N)H(2N-4)	TRICYCLOPARAFFINS	6.6	
C(N)H(2N-6)	TETRACYCLOPARAFFINS	.0	
C(N)H(2N-8)	PENTACYCLOPARAFFINS	.0	
C(N)H(2N-10)	HEXACYCLOPARAFFINS	.0	
C(N)H(2N-12)	HEPTACYCLOPARAFFINS	.0	
	SATURATES		76.2
MONOAROMATICS			
C(N)H(2N-6)	ALKYLBENZENES	12.0	
C(N)H(2N-8)	BENZOCYCLOPARAFFINS	10.5	
C(N)H(2N-10)	BENZODICYCLOPARAFFINS	.3	
DIAROMATICS			
C(N)H(2N-12)	NAPHTHALENES	1.1	
C(N)H(2N-14)		.0	
C(N)H(2N-16)		.0	
TRIAROMATICS			
C(N)H(2N-18)		.0	
C(N)H(2N-22)		.0	
TETRAAROMATICS			
C(N)H(2N-24)		.0	
C(N)H(2N-28)		.0	
	AROMATICS		23.8
C(N)H(2N-4)S	THIOPHENES	.0	
C(N)H(2N-10)S	BENZOTHIOPENES	.0	
C(N)H(2N-16)S	DIBENZOTHIOPHENES	.0	
C(N)H(2N-22)S	NAPHTHOBENZOTHIOPHENES	.0	
	SULFUR COMPOUNDS		.0

CALCULATED %C= 86.8 %H= 13.2 %THIOPHENIC S= .00
AVERAGE C#= 12.6 AVERAGE MW= 173.1

PLEASE NOTE--
SAMPLE TYPES CORRECTLY ANALYZED
1. C12 TO C36, 250 DEG F TO 1050 DEG F HYDROCARBONS
2. OLEFIN-FREE HYDROCARBONS
3. LESS THAN 5% OXYGEN, NITROGEN, OR SULFUR COMPS.
ONLY LISTED TYPES ARE CONSIDERED, ALL OTHERS IGNORED

MATRIX COMPOSITION:

MTX	%	MTX	%	MTX	%	MTX	%
1	71.8	2	23.9	3	4.3	4	.0
5	.0	6	.0	7	.0	8	.0

Matrix selection based on distillation data

TABLE 36. Analysis of coal-liquid fuel 2987 aged 4 weeks at 80° C by 22-component hydrocarbon type method

ANALYTICAL DIVISION
MASS SPECTROMETRY LABORATORY

PROGRAM 34 CALC. AT 11:22: 0 ON 6/23/89
CUSTOMER: WH ACCT NO: BO6817

RUN: 05159B. ACQU. AT 00:00:0 ON 5/15/89.
SAMPLE: 05159B10. 5/15/89. ANAL. OF FUEL 2987-80-10, AGED 4 WKS 80 C

C(N)H(2N+2)	PARAFFINS	4.6	
C(N)H(2N)	MONOCYCLOPARAFFINS	44.3	
C(N)H(2N-2)	DICYCLOPARAFFINS	21.1	
C(N)H(2N-4)	TRICYCLOPARAFFINS	9.1	
C(N)H(2N-6)	TETRACYCLOPARAFFINS	.0	
C(N)H(2N-8)	PENTACYCLOPARAFFINS	.0	
C(N)H(2N-10)	HEXACYCLOPARAFFINS	.0	
C(N)H(2N-12)	HEPTACYCLOPARAFFINS	.0	
		SATURATES	79.1
MONOAROMATICS			
C(N)H(2N)	ALKYLBENZENES	12.0	
C(N)H(2N-8)	BENZOCYCLOPARAFFINS	6.7	
C(N)H(2N-10)	BENZODICYCLOPARAFFINS	.9	
DIAROMATICS			
C(N)H(2N-12)	NAPHTHALENES	1.3	
C(N)H(2N-14)		.0	
C(N)H(2N-16)		.0	
TRIAROMATICS			
C(N)H(2N-18)		.0	
C(N)H(2N-22)		.0	
TETRAAROMATICS			
C(N)H(2N-24)		.0	
C(N)H(2N-28)		.0	
		AROMATICS	20.9
C(N)H(2N-4)S	THIOPHENES	.0	
C(N)H(2N-10)S	BENZOTHIOPENES	.0	
C(N)H(2N-16)S	DIBENZOTHIOPHENES	.0	
C(N)H(2N-22)S	NAPHTHOBENZOTHIOPHENES	.0	
		SULFUR COMPOUNDS	.0

CALCULATED %C= 86.7 %H= 13.3 %THIOPHENIC S= .00
AVERAGE C#= 12.7 AVERAGE MW= 173.7

PLEASE NOTE--
SAMPLE TYPES CORRECTLY ANALYZED
1. C12 TO C36, 250 DEG F TO 1050 DEG F HYDROCARBONS
2. OLEFIN-FREE HYDROCARBONS
3. LESS THAN 5% OXYGEN, NITROGEN, OR SULFUR COMPS.
ONLY LISTED TYPES ARE CONSIDERED, ALL OTHERS IGNORED

MATRIX COMPOSITION:

MTX	%	MTX	%	MTX	%	MTX	%
1	70.3	2	24.7	3	5.0	4	.0
5	.0	6	.0	7	.0	8	.0

Matrix selection based on distillation data

TABLE 37. Analysis of coal-liquid fuel 2987 from oxidation stability test (ASTM D 2274) by 22-component hydrocarbon type method

ANALYTICAL DIVISION
MASS SPECTROMETRY LABORATORY

PROGRAM 34 HC22_2 CALC. AT 12:47:34 ON 6/29/89
CUSTOMER: WH ACCT NO: 806817

RUN: 06019A. ACQU. AT 00:00:0 ON 6/1/89.
SAMPLE: 06019A12. 6/1/89. FUEL 2987 FROM OX. STAB. TEST. 40 HRS

C(N)H(2N+2)	PARAFFINS	6.0	
C(N)H(2N)	MONOCYCLOPARAFFINS	41.0	
C(N)H(2N-2)	DICYCLOPARAFFINS	21.2	
C(N)H(2N-4)	TRICYCLOPARAFFINS	7.6	
C(N)H(2N-6)	TETRACYCLOPARAFFINS	.0	
C(N)H(2N-8)	PENTACYCLOPARAFFINS	.0	
C(N)H(2N-10)	HEXACYCLOPARAFFINS	.0	
C(N)H(2N-12)	HEPTACYCLOPARAFFINS	.0	
	SATURATES		75.8
MONOAROMATICS			
C(N)H(2N-6)	ALKYLBENZENES	12.3	
C(N)H(2N-8)	BENZOCYCLOPARAFFINS	9.1	
C(N)H(2N-10)	BENZODICYCLOPARAFFINS	1.3	
DIAROMATICS			
C(N)H(2N-12)	NAPHTHALENES	1.5	
C(N)H(2N-14)		.0	
C(N)H(2N-16)		.0	
TRIAROMATICS			
C(N)H(2N-18)		.0	
C(N)H(2N-22)		.0	
TETRAAROMATICS			
C(N)H(2N-24)		.0	
C(N)H(2N-28)		.0	
	AROMATICS		24.2
C(N)H(2N-4)S	THIOPHENES	.0	
C(N)H(2N-10)S	BENZOTHIOPENES	.0	
C(N)H(2N-16)S	DIBENZOTHIOPHENES	.0	
C(N)H(2N-22)S	NAPHTHOBENZOTHIOPHENES	.0	
	SULFUR COMPOUNDS		.0

CALCULATED %C= 86.8 %H= 13.2 %THIOPHENIC S= .00
AVERAGE C#= 12.6 AVERAGE MW= 173.1

PLEASE NOTE--
SAMPLE TYPES CORRECTLY ANALYZED
1. C12 TO C36, 250 DEG F TO 1050 DEG F HYDROCARBONS
2. OLEFIN-FREE HYDROCARBONS
3. LESS THAN 5% OXYGEN, NITROGEN, OR SULFUR COMPS.
ONLY LISTED TYPES ARE CONSIDERED. ALL OTHERS IGNORED

MATRIX COMPOSITION:

MTX	%	MTX	%	MTX	%	MTX	%
1	71.8	2	23.9	3	4.3	4	.0
5	.0	6	.0	7	.0	8	.0

Matrix selection based on distillation data

The two fresh fuel samples were analyzed by field ionization mass spectrometry to provide an independent check of the results from the previous HC-22 analyses on these fuels. The FI spectra were recorded with a Kratos MS-50 high resolution mass spectrometer (Kratos Analytical Instruments) with sample introduction through an all-glass expansion volume inlet (R. J. Brunfeldt Co.) at a temperature of 300° C. The ion-source temperature was 250° C. A field-desorption emitter (Linden ChroMasSpec) operated at a potential of 10 KV was used for ion formation, and masses were separated at a dynamic resolving power of approximately 3,000. Twenty spectra from one sample load were recorded at a scan rate of 100 seconds/decade. Intensities from all 20 spectra were summed to give one spectrum with better signal-to-noise ratio.

Table 38 shows results from the FI spectra recorded for fresh fuel 2955. To simplify the output, only relative intensities for even-mass peaks, representing the most abundant isotopic molecular ions, are tabulated, i.e., isotope peaks have been omitted. The table is arranged according to nominal mass Z series (NMZ), which classify ions by molecular mass and intensity into homologous series. Thus, relative intensities under the +2 NMZ column heading correspond to C_nH_{2n+2} homologues (paraffins) and those under the -6 NMZ heading to C_nH_{2n-6} homologues, e.g., alkylbenzenes. The sum of all intensities has been normalized to 1000. Although intensities have not been multiplied by sensitivity factors, a good estimate of relative abundance of a homologue in a given series with respect to others in the same series can be obtained from its relative intensity. This is a reasonable assumption because relative molar sensitivities are known to be fairly constant for homologues in a series. Thus, in the +2 NMZ series, the homologue of molecular mass 156 corresponding to $C_{11}H_{24}$ and having a relative intensity of 99.41 is the most abundant member of that series. (In general, molecular ions in nominal-mass FI spectra represent more than one isomer and possibly more than one compound type. For example, m/z 156 in the spectrum could well represent more than one paraffin isomer of elemental composition $C_{11}H_{24}$. The possibility also exists that m/z 156 corresponds to one or more naphthalenes having an elemental composition of $C_{12}H_{12}$. However, naphthalenes are relatively minor components of fuel 2955, as shown by the high-resolution mass spectra recorded previously. Therefore, their presence in fuel 2955 is neglected.)

Although uncorrected intensities in FI spectra provide good estimates of relative abundances of homologues in a given series, it is not true that abundances of homologues in different series can be compared without including sensitivity factors in the calculations. Thus in table 38, abundances of homologues in the 0 NMZ series (monocycloparaffins) cannot be compared with those in the +2 series because relative molar sensitivities of homologues in the two series are significantly different.

TABLE 38. - Analysis of fresh fuel 2955 by field ionization mass spectrometry

08079Z. 8/7/89. ANALYSIS OF FRESH FUEL 2955 BY FI/MS

REL I	MASS	NMZ NO./REL I						
		-10	-8	-6	-4	-2	0	+2
0.00	100							0.00
0.00	102	0.00						
0.00	104		0.00					
27.91	106			27.91				
0.00	108				0.00			
0.00	110					0.00		
6.25	112						6.25	
0.00	114							0.00
0.00	116	0.00						
0.00	118		0.00					
93.39	120			93.39				
0.00	122				0.00			
0.00	124					0.00		
19.54	126						19.54	
17.77	128							17.77
0.00	130	0.00						
0.82	132		0.82					
87.40	134			87.40				
0.00	136				0.00			
1.28	138					1.28		
39.12	140						39.12	
72.66	142							72.66
0.00	144	0.00						
8.59	146		8.59					
53.30	148			53.30				
0.00	150				0.00			
5.98	152					5.98		
43.05	154						43.05	
99.41	156							99.41
0.00	158	0.00						
15.92	160		15.92					
29.08	162			29.08				
0.00	164				0.00			
11.09	166					11.09		
33.53	168						33.53	
64.92	170							64.92
0.00	172	0.00						
16.46	174		16.46					
13.37	176			13.37				
0.00	178				0.00			
16.01	180					16.01		
34.75	182						34.75	
40.95	184							40.95
0.43	186	0.43						

TABLE 38. - Analysis of fresh fuel 2955 by field ionization mass spectrometry (contd)

9.63	188		9.63						
8.08	190			8.08					
0.57	192				0.57				
11.36	194					11.36			
29.82	196						29.82		
36.68	198							36.68	
0.00	200	0.00							
2.82	202		2.82						
3.11	204			3.11					
0.00	206				0.00				
4.50	208					4.50			
13.30	210						13.30		
15.45	212							15.45	
0.00	214	0.00							
0.18	216		0.18						
0.00	218			0.00					
0.00	220				0.00				
0.00	222					0.00			
6.97	224						6.97		
3.69	226							3.69	
0.00	228	0.00							
0.00	230		0.00						
0.00	232			0.00					
0.00	234				0.00				
0.00	236					0.00			
0.66	238						0.66		
0.22	240							0.22	
SUM		SUM	SUM	SUM	SUM	SUM	SUM	SUM	TOTAL
1000.00		0.43	54.42	315.63	0.57	50.22	226.99	351.75	1000.00

Similar comments apply to the FI data obtained for fresh fuel 2987 presented in table 39. Even though the relative intensities cannot be used to provide an overall quantitative analysis of the fuel without including sensitivity factors, the data can be used to make a comparison of relative molar concentrations of homologues in the same series between fuels 2955 and 2987. Thus, the paraffin concentration for fuel 2955 is much higher than for fuel 2987, as shown by the ratio of the respective +2 NMZ column sums: 351.75/2.92 = 120.5. By the same reasoning, the monocycloparaffin concentration in the two fuels is about the same; the ratio is 226.99/210.92 = 1.08 for the 0 NMZ column sums. Fuel 2955 contains significantly lower concentrations of dicycloparaffins (-2 NMZ) and tricycloparaffins (-4 NMZ) than fuel 2987: 50.22/248.09 = 0.202 and 0.57/52.59 = 0.011, respectively, for the two ratios. On the other hand, fuel 2955 contains more alkylbenzenes (315.63/128.06 = 2.46), less benzocycloparaffins (54.42/317.44 = 0.17), and less benzodicycloparaffins (0.43/39.97 = 0.011) than fuel 2987, as shown by the respective sums for the -6 NMZ, -8 NMZ, and -10 NMZ columns in tables 38 and 39.

Significant differences between the compositions of the two fuels are also apparent in the distributions of homologues in the same series. Thus, for example, alkylbenzenes are distributed toward lower molecular weights in fuel 2955 as compared to the distribution in fuel 2987. Other differences in the distributions can be seen by comparing results in tables 38 and 39.

Good qualitative agreement is found when results from the FI analyses on the two fresh fuels are compared with results from the 22-component analyses. However, significant quantitative differences exist between the two sets of results. Part of the discrepancy may arise from the presence of components having carbon numbers less than twelve in relatively high concentrations in the two fuels, as is evident from the FI data given in tables 38 and 39. According to limitations on the 22-component analysis, only compound types with carbon numbers in a range from C_{12} to C_{36} are correctly analyzed.

SUMMARY AND CONCLUSIONS

Results from a study of the storage and thermal stabilities of a JP-8 fuel produced from the Great Plains Gasification Plant liquid by-product streams were compared with similar results for a conventional petroleum-derived JP-8 fuel. Initial characterization and simulated distillation data for the two fuels indicated the coal-derived fuel contained more lower boiling material, a slight color, a high filtration time, and a high particulate content (the latter three properties being due to some suspended clay, most likely). Nevertheless, for the most part both fuels met specification tests for JP-8.

Both fuels exhibited good oxidation stability according to test ASTM D 2274 with the coal-derived fuel showing less sediment and color formation but somewhat higher peroxide content. Storage stability tests (aging at 80° C under 100 psig oxygen) gave the same results through 3 weeks of aging. However, between the third and fourth weeks the coal-derived fuel deteriorated rapidly and exceeded the petroleum-derived reference fuel in color and sediment formation as well as peroxide content.

TABLE 39. - Analysis of fresh fuel 2987 by field ionization mass spectrometry

08079Y. 8.7/89. ANALYSIS OF FRESH FUEL 2987 BY FI/MS

REL I	MASS	NMZ NO./REL I						
		-10	-8	-6	-4	-2	0	+2
0.00	80				0.00			
0.00	82					0.00		
0.65	84						0.65	
0.00	86							0.00
0.00	88	0.00						
0.00	90		0.00					
2.95	92			2.95				
0.00	94				0.00			
0.00	96					0.00		
26.93	98						26.93	
0.00	100							0.00
0.00	102	0.00						
0.00	104		0.00					
14.07	106			14.07				
0.00	108				0.00			
0.00	110					0.00		
66.92	112						66.92	
0.19	114							0.19
0.00	116	0.00						
0.27	118		0.27					
19.12	120			19.12				
0.00	122				0.00			
0.97	124					0.97		
48.44	126						48.44	
0.00	128							0.00
0.00	130	0.00						
43.48	132		43.48					
21.39	134			21.39				
0.00	136				0.00			
58.64	138					58.64		
34.42	140						34.42	
0.00	142							0.00
0.00	144	0.00						
68.42	146		68.42					
16.25	148			16.25				
0.00	150				0.00			
56.90	152					56.90		
12.96	154						12.96	
0.93	156							0.93
0.00	158	0.00						
79.25	160		79.25					
17.12	162			17.12				
0.00	164				0.00			
52.93	166					52.93		

TABLE 39. - Analysis of fresh fuel 2987 by field ionization mass spectrometry (contd)

8.80	168						8.80		
0.45	170							0.45	
5.43	172	5.43							
60.82	174		60.82						
17.14	176			17.14					
10.09	178				10.09				
33.55	180					33.55			
5.99	182						5.99		
0.46	184							0.46	
18.21	186	18.21							
38.10	188		38.10						
16.88	190			16.88					
25.72	192				25.72				
25.53	194					25.53			
4.38	196						4.38		
0.00	198							0.00	
11.97	200	11.97							
20.31	202		20.31						
2.79	204			2.79					
14.10	206				14.10				
16.20	208					16.20			
1.42	210						1.42		
0.43	212							0.43	
4.36	214	4.36							
5.80	216		5.80						
0.35	218			0.35					
2.49	220				2.49				
2.39	222					2.39			
0.00	224						0.00		
0.46	226							0.46	
0.00	228	0.00							
1.00	230		1.00						
0.00	232			0.00					
0.19	234				0.19				
0.99	236					0.99			
0.00	238						0.00		
0.00	240							0.00	
SUM		SUM	SUM	SUM	SUM	SUM	SUM	SUM	TOTAL
1000.00		39.97	317.44	128.06	52.59	248.09	210.92	2.92	1000.00

After separation of the coal-derived fuel into acid, base, and neutral fractions, storage stability tests on the neutrals, neutrals + acids, neutrals + bases, and neutrals + acids + bases (reconstituted fuel) showed large amounts of sediments formed after 4 weeks aging in each case with the neutrals alone producing the largest quantity.

Both fuels easily met specifications in terms of thermal stability testing with the coal-derived fuel showing a higher breakpoint temperature. Extended JFTOT runs were conducted at temperatures slightly above the breakpoint to generate filterable sediment and tube deposit samples for analyses.

Infrared analysis of a sample of sediment from the coal-liquid derived JP-8 fuel storage stability tests was not very definitive; however, the spectrum was similar to that of the acid fraction separated from the fresh fuel. Separation of the sediment sample using NIPER's HPLC acid subfractionation method indicated the sediment was composed primarily of carboxylic acids and difunctional acids.

Mass spectra of the filterable sediments and JFTOT-tube deposits formed during extended thermal stressing runs of the coal-derived and petroleum-derived fuels were remarkably similar, indicating that the same or similar compound types were responsible for solids formation in both fuels.

When spectra of the filterable sediment from either fuel were compared with those of the tube deposit from the same fuel, a number of similarities were found as well as some significant differences. Both sets of spectra showed molecular- and fragment-ion peaks for aromatic and nonaromatic hydrocarbons and for compounds containing one to three oxygens. Strong peaks were observed in the spectra of the filterable sediment corresponding to aromatic compounds containing one nitrogen. These peaks were much weaker or absent in the spectra from the tube deposit. No spectra of the sediment or tube deposit from either fuel showed any more than traces of sulfur-containing compounds.

An intense, nonaromatic fragment ion containing three oxygens was identified in the spectra of the tube deposits from both fuels. This ion was also found in the spectra of the filterable sediments from both fuels although its intensity was much weaker. The ion could not be correlated with a molecular ion from any particular compound type, but it may have originated from an alcohol, ether, or some other type that does not produce a significant molecular ion.

A 22-component hydrocarbon type mass spectral analysis method applied to fresh samples of the two fuels and samples of the fuels after stability testing was not sufficiently sensitive to detect any significant changes in the composition of either fuel. On the other hand, very significant differences were evident in the compositions of the petroleum-derived fuel and the coal-derived fuel when one was compared to the other. Field ionization mass spectral analysis of fresh samples of the two fuels gave results in good qualitative agreement with the 22-component method results. Comparison of the two methods on a quantitative basis was not possible because of the lack of sensitivity factors for the FI/MS data. However, the FI/MS analysis did indicate relatively high concentrations of components with carbon numbers less than twelve in both fuels which are outside the range C_{12} to C_{36} for which the 22-component method is strictly applicable.

Although neither the analyses of the fresh, aged, and stressed fuels nor the structural information obtained through mass-spectral analysis of the filterable sediments and tube deposits led to identification of any specific precursors responsible for solids formation in the two fuels in the study, the results presented do demonstrate the potential of the methods for studying the mechanisms leading to fuel degradation under conditions of high temperature, such as those encountered in turbine engines.

REFERENCES

1. Furlong, M., J. Fox, J. Masin, AFWAL-TR-87-2042, "Production of Jet Fuels From Coal-Derived Liquids, Vol. IX, Results of Bench-Scale and Pilot Plant Testing," June 1989.

2. Coordinating Research Council, CRC Literature Survey on the Thermal Oxidation Stability of Jet Fuel, CRC Report No. 509, April 1979, p. 53-68.

3. Coordinating Research Council, Research Technique for Thermal Stability by Modified Jet Fuel Thermal Oxidation Test (JFTOT), CRC Report No. 496, June 1978, p. 1-7.

4. Whisman, M. L., F. O. Cotton, J. W. Goetzinger, and C. C. Ward. Radiotracer Study of Turbine Aircraft Fuel Stability, Bureau of Mines Report of Investigation 7493, March 1971.

5. Bhan, O. K., D. W. Brinkman, J. B. Green, and B. Carley, "Storage Stability of Marine Diesel Fuels," Fuel, v. 66, p. 1200, September 1987.

6. Grigsby, R. D., Sturm, G. P., Jr., Green, J. B., Goetzinger, J. W., and Kamin, R. A., PREPRINTS, Div. Petro. Chem., ACS, 34 (4), 825-831 (1989).

7. Monthly Report for September, 1989: IITRI/NIPER Project SGP18, Work Performed for the Naval Air Propulsion Center and the U.S. Department of Energy Under Cooperative Agreement DE-FC22-83FE60149, October 12, 1989.

8. Schronk, L. R., Grigsby, R. D., and Scheppele, S. E., Anal. Chem., 54, 748-755 (1982).

9. Teeter, R. M. Mass Spectrometry Reviews 1985, 4, 123-143.

10. Gallegos, E. G., Green, J. W., Lindeman, L. P., LeTourneau, R. L., Teeter, R. M. Anal. Chem. 1967, 39, 1833.

APPENDIX A

SIMULATED DISTILLATION DATA FOR JP-8
FUELS 2955 AND 2987

ASTM D-2887 REPORT

SAMPLE: **2955 JP-8 JET FUEL** BOTTLE#:3

SAMPLER INJECTION @ 14:05 OCT 14, 1988

% OFF	DEG F	% OFF	DEG F
IBP	240		
1	246	51	398
2	259	52	401
3	271	53	404
4	277	54	406
5	282	55	408
6	286	56	411
7	290	57	414
8	293	58	417
9	299	59	418
10	302	60	420
11	305	61	421
12	309	62	423
13	314	63	426
14	317	64	428
15	319	65	431
16	322	66	434
17	324	67	437
18	327	68	440
19	329	69	442
20	331	70	444
21	333	71	446
22	335	72	449
23	337	73	451
24	340	74	453
25	343	75	455
26	344	76	457
27	346	77	460
28	347	78	463
29	349	79	467
30	352	80	471
31	354	81	475
32	356	82	478
33	358	83	481
34	361	84	483
35	363	85	486
36	365	86	488
37	368	87	491
38	370	88	495
39	372	89	500
40	375	90	504
41	378	91	508
42	380	92	513
43	383	93	517
44	384	94	521
45	386	95	527
46	387	96	535
47	388	97	544
48	391	98	555
49	394	99	577
50	396	FBP	601

ASTM D-2887 REPORT

SAMPLE:JP-8 2987 BOTTLE#:3

SAMPLER INJECTION @ 16:58 MAR 8, 1989

% OFF	DEG F	% OFF	DEG F
IBP	179		
1	185	51	389
2	199	52	392
3	213	53	395
4	215	54	397
5	216	55	399
6	218	56	400
7	228	57	402
8	238	58	406
9	242	59	409
10	245	60	412
11	248	61	415
12	252	62	418
13	256	63	421
14	263	64	424
15	268	65	428
16	270	66	432
17	272	67	435
18	277	68	438
19	282	69	441
20	286	70	444
21	290	71	447
22	294	72	451
23	297	73	453
24	301	74	455
25	306	75	458
26	310	76	461
27	314	77	465
28	318	78	468
29	323	79	472
30	327	80	475
31	332	81	478
32	335	82	482
33	337	83	485
34	341	84	488
35	345	85	491
36	349	86	495
37	353	87	499
38	357	88	503
39	359	89	507
40	361	90	511
41	363	91	515
42	364	92	520
43	366	93	525
44	368	94	532
45	372	95	540
46	376	96	548
47	379	97	559
48	382	98	574
49	384	99	591
50	387	FBP	610

☆U.S.Government Printing Office: 1990—748-056/24367